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LXV.—*A Comparison of Some of the Physical Properties of the Alkali Cyanates and Azides.*

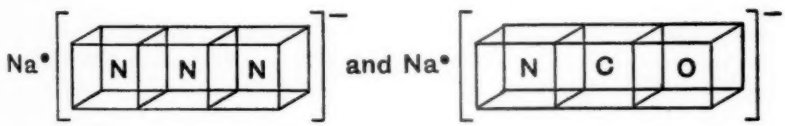
By JOHN ARNOLD CRANSTON and ALEXANDER YOUNG LIVINGSTONE.

ACCORDING to modern ideas of the structure of atoms, the chemical and physical properties of elements depend on the number and arrangement of the outer electrons of the atom of the element.

The cyanate and azide ions have the same number of external electrons in their alkali salts, and it is possible that these electrons are arranged in the same way. According to the older views of valency, however, it was more common to find a ring structure assigned to azides and a straight-chain structure to cyanates. The constitutional formulæ were thus represented as

$$Na—N\!<\!\begin{matrix}N\\ \|\\ N\end{matrix} \text{ and } Na—O—C\equiv N.$$

The appearance of these formulæ does not suggest any close resemblance between the physical properties of the compounds. The formulæ suggested by the octet theory for these compounds are



and their great similarity suggests a close resemblance of the physical properties of these two salts. As far as previously published data go, the evidence favours the formulæ of the octet theory, and it was the object of this investigation to supplement the data, which were rather meagre.

Preparation of Salts.—The following salts were prepared and purified according to the recognised text-book methods: Potassium cyanate, potassium azide; sodium cyanate, sodium azide.

Investigation of Physical Properties.—1. *Densities of solutions.* Since comparative, rather than absolute, values for the data for the various physical properties were aimed at, great care was taken to carry out all measurements for the cyanates and azides under uniform conditions.

A pyknometer of about 17 c.c. capacity was used for the determination of the densities of the solutions that were made up. Cyanates are decomposed by water, but the rate of decomposition

is greatly reduced in presence of alcohol. The solvent employed for the various dilutions was accordingly a mixture of about equal volumes of alcohol and water. All measurements were carried out after the pyknometer containing the solutions had been immersed in a thermostat at 16° for 20 minutes. The results are in Table I.

2. *The refractive indices of* the various solutions were determined by the Abbé refractometer at the same temperature at which their densities had been observed. The results are also in Table I.

TABLE I.

Strength of soln.	Density.		Refractive index.		Density.		Refractive index.	
	KN_3 soln.	KCNO soln.	KN_3 soln.	KCNO soln.	NaN_3 soln.	NaCNO soln.	NaN_3 soln.	NaCNO soln.
N	—	—	—	—	0·979	0·978	1·371	1·374
$N/2$	0·956	0·956	1·362	1·362	0·954	0·954	1·362	1·364
$N/4$	0·948	0·948	1·360	1·360	0·946	0·946	1·359	1·360
$N/8$	0·941	0·941	1·359	1·359	0·941	0·941	1·351	1·352
$N/16$	0·938	0·938	1·357	1·358	—	—	—	—

3. *The densities of the crystalline salts* were determined by immersing a weighed quantity, about 5 g., in benzene contained in an ordinary specific gravity bottle. Previous experiment had shown that the solubility of these salts in benzene at room temperature is less than 0·1 g. in 100 c.c. Too great reliance cannot be placed on the value obtained for sodium cyanate, owing to the instability of this salt; although different determinations gave consistent values, there was always a detectable quantity of carbonate formed during the measurements. The mean values obtained were as follows:

TABLE II.

	KN_3.	KCNO.	NaN_3.	NaCNO.
Density at 20°	2·056	2·056	1·846	1·937

4. *Determination of solubilities.* The solubilities of these salts in alcohol ($d^{17°}$ 0·799) were determined at 0° and at the boiling point of the saturated solution. Definite volumes of the solutions were withdrawn by means of a pipette, and the solutions weighed. The cyanates were estimated volumetrically by the method suggested by Masson (*Chem. News*, 1906, **90**, 5, 17), the azides by the method suggested by Raschig (*Chem. Ztg.*, 1908, 1203).

Solubilities were also measured in 20% water and 80% alcohol at 0° and at the boiling point of the saturated solution, and as well as in benzene at the boiling point.

TABLE III.

Solvent.	Weight dissolved in 100 g. of solvent. KN_3.	KCNO.	NaN_3.	NaCNO.
Alcohol at 0°	0·16	0·16	0·22	0·22
Alcohol at b. p.	0·54	0·53	0·46	0·52
80% Alcohol, 20% Water at 0°	1·8	1·9	—	—
„ „ at b. p.	5·9	6·2	—	—
Benzene at b. p.	0·15	0·18	0·10	0·13

5. *Conductivity of solutions.* A preliminary attempt to determine the hydrion concentration of a solution of an alkali azide by the electrometric method showed that the salt is decomposed by water in presence of platinum black. This decomposition is very rapid when hydrogen is present occluded in the platinum. Nitrogen and ammonia are liberated, and the solution becomes progressively more alkaline. Apparently the reaction is as follows: $3KN_3 + 3H_2O = 3KOH + 4N_2 + NH_3$.

Since cyanates are also decomposed by water, the solvent used in the conductivity measurements was methyl alcohol ($d^{20°}$ 0·789).

The following results were obtained.

TABLE IV.

Strength of solution.	Equivalent conductivity at 25°. NaN_3.	NaCNO.	KN_3.	KCNO.
N/10	58·7	58·3	62·8	60·3
N/20	69·0	68·0	68·0	68·6
N/40	78·8	75·6	77·2	77·6
N/80	90·4	88·0	88·8	88·8

The investigations of Carrara (*Gazzetta*, 1896, **26**, i, 134) have shown that the ionic conductivities of sodium and potassium are approximately equal in methyl alcohol.

Discussion of Results.

It will be seen from the above tables that all the physical properties investigated have shown the great resemblance between sodium azide and sodium cyanate on the one hand and potassium azide and potassium cyanate on the other. This, taken in conjunction with the similarity of crystal structure noted by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543), is strong evidence that the arrangement of electrons and atoms in the cyanate and azide ions is the same.

ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, October 31st*, 1925.]

LXVI.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part VI. Rotatory Powers of Phenyl, o, m, p-Tolyl and β-Naphthyl Derivatives of d-Camphorimide and d-Camphoramic Acid.*

By Bawa Kartar Singh and Amar Nath Puri.

The rotatory powers of a number of aryl derivatives of *d*-camphorimide and *d*-camphoramic acid in three solvents at different concentrations have been studied with the object of finding some relation between their optical activity and chemical constitution, and the following conclusions drawn:

1. Substitution of an aryl group for the imido-hydrogen atom increases the rotatory power, and more so than does substitution of the benzyl group (Singh and Biswas, J., 1924, **125**, 1895).

2. The influence of the solvent on the rotatory power is considerable in the case of derivatives of *d*-camphoramic acid, but it is small in the case of those of *d*-camphorimide.

The order of the dielectric constants of the solvents employed is methyl alcohol (32·5) > ethyl alcohol (26·0) > acetone (21·2). In most cases (see Tables I and II), the order of the rotatory powers in these solvents is methyl alcohol > ethyl alcohol > acetone. It thus appears that in the case of these solvents the order of the rotatory powers generally runs parallel to their dielectric constants, although there is no direct proportionality between them.

3. The relative magnitude of the rotatory powers of phenyl and tolyl derivatives of *d*-camphorimide and *d*-camphoramic acid varies with the nature of the solvent and the concentration of the solution, as is seen in Tables I and II.

Table I.

Derivatives of *d*-camphoramic acid.	$[M]_D$. 2% Solution.			1% Solution.		
	EtOH.	MeOH.	Me_2CO.	EtOH.	MeOH.	Me_2CO.
Phenyl	+131°	+150°	+101°	+133°	+152°	+101°
o-Tolyl	144	146	98	158	151	91
m-Tolyl	118	140	89	122	147	92
p-Tolyl	144	167	120	146	170	122
	o = *p* > un. > *m*;	*p* > un. > *o* > *m*;	*p* > un. > *o* > *m*;	*o* > *p* > un. > *m*;	*p* > un., *o* and *m*; *p* > un. > *m* and *o*.	

For none of these derivatives do Frankland's and Cohen's rules hold.

TABLE II.

	$[M]_D$.					
	1·5% Solution.			0·75% Solution.		
Derivatives of *d*-camphorimide.	EtOH.	MeOH.	Me_2CO.	EtOH.	MeOH.	Me_2CO.
Phenyl	+48°	+49°	+44°	+48°	+52°	+48°
o-Tolyl	45	46	36	53	56	43
m-Tolyl	48	48	50	55	53	37
p-Tolyl	46	52	54	42	48	49

In the case of the derivatives of *d*-camphorimide, the differences in the rotatory powers of the position isomerides are in many cases so small, and within the limits of experimental error, that it is not permissible to draw any general conclusions.

The variation of the optical rotatory power with concentration was more fully investigated in the case of *d*-camphor-*p*-tolylamic acid in ethyl and methyl alcohols for concentrations varying from 1 to 10%. In both solvents the rotatory power decreases as the concentration increases. This may be due to the decrease in the number of optically active molecules in more concentrated solutions owing to molecular association.

4. The rotatory power of a cyclic compound is usually considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-*cyclo*pentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, **140**, 1205), and the hexahydrophthalic acids have much lower rotatory powers than their anhydrides (Werner, *Ber.*, 1899, **32**, 3046). This rule is more strikingly borne out in the case of derivatives of monosaccharides. The rotatory power of *d*-mannitol is $[\alpha]_D^{20^\circ} = -0{\cdot}2^\circ$ (Fischer, *Ber.*, 1890, **23**, 3684), whereas that of *d*-mannonolactone is +53·8° (Fischer, *Ber.*, 1889, **22**, 3219). The high rotatory power of most of the sugars as compared with the corresponding polyhydric alcohols is a proof of the ring structure of the former. The increase which is brought about in the rotatory power of sugar alcohols by boric acid is attributed to the formation of ring complexes. Camphoramic acids and their anhydrides form an exception to the rule, the acids having $[M]_D$ 89·45° (α), 119·4° (β) in ethyl alcohol, whilst the anhydride has $[M]_D$ 10·99°. It was pointed out (J., 1924, **125**, 1895) that opening the rings of *d*-camphorimide and its derivatives increases the rotation considerably; *e.g.* the following are values of $[M]_D$ in ethyl alcohol: camphorbenzylimide 30·19°, camphorbenzylamic acid 99·88°, camphor-*m*-nitrobenzylimide 31·92°, camphor-3-nitrobenzylamic acid 106·7°. The differences in the molecular rotatory powers of the aryl derivatives

of *d*-camphorimide and *d*-camphoramic acid are of the same order as of the foregoing substances, except in the case of β-naphthyl derivatives, for which the difference is much greater; *e.g.*, the following are values of $[M]_D$ in ethyl alcohol: camphor-β-naphthylimide 60°, *d*-camphor-β-naphthylamic acid 229°. From the foregoing instances it may be concluded that when an open-chain, optically active compound is transformed into a ring compound, there is a marked change (not necessarily an increase) in the rotatory power.

EXPERIMENTAL.

Aryl Derivatives of d-*Camphoramic Acid.*—d-*Camphorphenylamic acid*, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NHPh$, was prepared by heating camphoric anhydride and aniline in molecular proportions in chloroform on the water-bath for 4—5 hours. The solid obtained on cooling crystallised from aqueous alcohol in needles, m. p. 209—210°. Auwers and Schleicher (*Annalen*, 1899, **309**, 341) give m. p. 203—204°.

d-*Camphor*-p-*tolylamic acid*, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_7H_7$, was prepared like the foregoing substance as leaflets, m. p. 214—215°. Wootton (J., 1910, **97**, 405), who obtained it by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150—180°, gives the melting point 212—214°, whereas Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219) give 201—209°.

d-*Camphor*-m-*tolylamic acid* was prepared by Wootton's method (*loc. cit.*) and purified by dissolving it in alcohol and adding animal charcoal. It was recrystallised as needles, m. p. 208—209°.

d-*Camphor*-o-*tolylamic acid*, prepared in the foregoing way, melted at 196—197°.

d-*Camphor*-β-*naphthylamic acid*, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_{10}H_7$, was prepared by both methods as white leaflets, m. p. 212—213°. The yield was, however, better when the condensation was carried out without any solvent.

N-*Aryl Derivatives of* d-*Camphorimide.*—These compounds were prepared by heating camphoric anhydride and the substituted amines in molecular proportions with the addition of a little anhydrous sodium sulphate in an oil-bath (215—230°) for 2 to 3 hours. The products of condensation were extracted with alcohol, decolorised by animal charcoal, and precipitated by adding water. They were twice recrystallised from aqueous alcohol, and gave the following melting points: phenyl, 117—118°; *o*-tolyl, 105—106°; *m*-tolyl, 121—122°; *p*-tolyl, 127—128°; β-naphthyl, 171—172°.

The tolyl and β-naphthyl derivatives of camphorimide were prepared by Wootton (*loc. cit.*) by boiling a solution of the corresponding *N*-substituted *d*-camphoramic acid in glacial acetic acid with acetyl chloride for 2 hours. Wootton gives the melting point

TABLE III.

Solvent.	Conc. (g./100 c.c.).	Temp.	α_D.	$[M]_D$.	Conc. (g./100 c.c.).	Temp.	α_D.	$[M]_D$.
	d-Camphorphenylamic acid.				*d*-Camphorphenylimide.			
EtOH	0·5265	26°	+0·51°	+133°	0·7693	18°	+0·29°	+48°
,,	1·0516	27	1·00	131	1·4950	19	0·56	48
MeOH	1·0025	22	1·11	152	0·7447	18	0·30	52
,,	2·0030	22	2·19	150	1·4765	17	0·56	49
Me_2CO	0·9775	23	0·72	101	0·7457	17	0·28	48
,,	2·0230	24	1·47	100	1·4755	18	0·50	44
	d-Camphor-*o*-tolylamic acid.				*d*-Camphor-*o*-tolylimide.			
EtOH	1·0155	26	1·11	158	0·7618	18	0·30	53
,,	2·0345	24	2·03	144	1·4925	19	0·49	45
MeOH	1·0140	22	1·06	151	0·6807	17	0·28	56
,,	1·9995	22	2·02	146	1·1772	18	0·40	46
Me_2CO	0·9099	22	0·57	91	0·6607	17	0·21	43
,,	2·0701	23	1·40	98	1·4585	17	0·39	36
	d-Camphor-*m*-tolylamic acid.				*d*-Camphor-*m*-tolylimide.			
EtOH	1·0210	23	0·86	122	0·7678	18	0·31	55
,,	1·9710	25	1·61	118	1·5135	19	0·53	48
MeOH	1·0130	22	1·03	147	0·7187	17	0·28	53
,,	1·7292	22	1·68	140	1·4374	18	0·51	48
Me_2CO	1·0325	22	0·66	92	0·5906	17	0·16	37
,,	2·0340	23	1·25	89	1·4565	18	0·54	50
	d-Camphor-*p*-tolylamic acid.				*d*-Camphor-*p*-tolylimide.			
EtOH	0·9970	27	1·01	146	1·0030	23	0·31	42
,,	1·9965	27	1·99	144	2·0070	24	0·68	46
,,	2·8994	17	2·91	145				
,,	4·0040	17	3·92	142				
,,	5·0140	17	4·86	140				
,,	5·9710	18	5·70	138				
,,	7·0395	18	6·58	135				
,,	8·0981	17	7·50	134				
,,	9·0550	18	8·16	130				
,,	10·0560	18	8·95	129				
MeOH	1·0035	22	1·18	170	0·7673	18	0·27	48
,,	2·0070	22	2·32	167	1·4580	17	0·56	52
,,	3·0130	18	3·40	163				
,,	4·0100	19	4·49	162				
,,	5·0671	17	5·26	150				
,,	10·0360	17	10·10	145				
Me_2CO	0·9510	24	0·80	122	0·7708	18	0·28	49
,,	2·0250	22	1·68	120	1·4700	18	0·59	54
	d-Camphor-β-naphthylamic acid.				*d*-Camphor-β-naphthylimide.			
EtOH	1·1505	14	1·62	229	0·9130	13	0·37	60
MeOH	1·0180	14	1·54	246	0·5100	15	0·21	61
Me_2CO	1·0530	15	1·38	213	0·8520	15	0·32	56

for the *o*-tolyl derivative 195—196°, which is obviously wrong. We also prepared this substance by his method and found the melting point 105—106°.

Before their rotatory powers were determined, the compounds were recrystallised three times in order to ensure their "optical" purity. Wootton has recorded the rotatory powers of these sub-

stances in acetone; his exact concentrations are not stated. In the case of derivatives of camphoramic acid, his values agree with ours, except in the case of the *p*-tolyl derivative, his value (107°) being lower than ours (120° to 122°, according to concentration). In the case of the *p*-tolyl derivative of *d*-camphorimide, his value ($[\alpha]_D$ 34°) is again lower than ours (49° to 54°, according to concentration).

The rotatory powers recorded in Table III were determined by dissolving a given weight of the substance in a solvent, and making up the solution to a definite volume. The readings were taken in a 2-dcm. tube within 45 minutes of making up the solution. There was no mutarotation.

The rotatory powers and dispersion ratios of *d*-camphorbenzylamic acid and *d*-camphor-*m*-nitrobenzylamic acid (higher-melting form) were omitted from Part V of this series (*loc. cit.*). They are given below for the sake of completeness.

Solvent.	Conc. (g./100 c.c.).	Temp.	Molecular rotatory powers. $[M]_{5893}$.	$[M]_{5780}$.	$[M]_{5461}$.	Dispersion ratios. $\alpha_{5461}/\alpha_{5893}$.
			d-Camphorbenzylamic acid.			
Chloroform	1·6193	23°	+92°	+95°	+108°	1·18
Acetone.....	1·9143	25	97	98	111	1·15
Ether.....	1·1590	21	89	92	107	1·21
Ethyl alcohol	3·3400	22	100	107	120	1·25
Methyl alcohol ...	1·2249	23	93	98	115	1·23
			d-Camphor-*m*-nitrobenzylamic acid, m. p. 179°.			
Chloroform	2·0485	23	80	83	94	1·18
Acetone.....	2·0676	25	95	97	111	1·13
Ethyl alcohol	2·8900	22	107	116	140	1·29
Methyl alcohol ...	1·5784	23	109	112	127	1·16

We wish to thank Mr. Sher Singh, B.Sc., for determining the rotatory powers of the β-naphthyl derivatives.

RAVENSHAW COLLEGE, CUTTACK,
BIHAR AND ORISSA, INDIA. [*Received, October 24th*, 1925.]

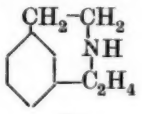
LXVII.—*Conditions of Formation of Rings Attached to the* o-, m-, *and* p-*Positions of the Benzene Nucleus. Part II. The Reduction of* m- *and* p-*Phenylenediacetonitrile.*

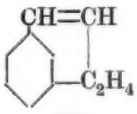
By ALAN FRANCIS TITLEY.

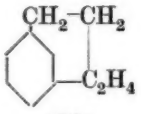
IN the course of some work on ring formation, the scope of which is outlined in Part I of this series (J., 1922, **121**, 1562), and a further account of which will be published shortly, it was found desirable

to repeat some investigations recently carried out by von Braun and his collaborators.

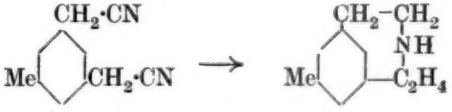
While attempting to prepare *m*-phenylene-ββ′-diethylamine by the reduction of *m*-phenylenediacetonitrile with sodium and alcohol, von Braun, Karpf, and Garn (*Ber.*, 1920, **53**, 98) claimed to have isolated a secondary amine of the composition $C_{10}H_{13}N$, to which they assigned the structure (I), where the heterocyclic ring is joined to the benzene nucleus in the meta-position. From this amine, by thermal decomposition of the quaternary dimethylammonium hydroxide with loss of dimethylamine and water, they stated that they obtained an unsaturated hydrocarbon and, by further reduction, a saturated hydrocarbon, to which they assigned the structures (II) and (III), respectively.


(I.)


(II.)


(III.)

More recently, von Braun and Engel (*Ber.*, 1925, **58**, 281) have described a homologue of this type, obtained in a similar manner by reducing 5-methyl-1 : 3-phenylenediacetonitrile.



The remarkable ease with which examples of this meta-ring system, generally supposed to be incapable of existence, are formed, together with their close structural relationship to the products it was hoped to obtain by the action of sodium on *m*-phenylenediacetic ester (Part I, *loc. cit.*), rendered a re-examination of this work desirable. It was not found possible, however, to confirm the results of von Braun and his co-workers and, in the present paper, evidence is brought forward to show that the amine (I) described by von Braun, Karpf, and Garn (*loc. cit.*) is in reality β-*m*-tolylethylamine (VII), and the unsaturated hydrocarbon derived from it *m*-methylstyrene (IX).*

The reduction of *m*-phenylenediacetonitrile, when carried out in accordance with the directions of these authors and using the same quantities and conditions, led to the formation of a mixture

* The proof of this paper was sent to Professor von Braun, and he wishes me to say that he has been engaged for some time in repeating the researches in question and has arrived at results which are identical with those contained in the present communication.—W. H. PERKIN.

of products, basic and non-basic. The non-basic substances were removed, together with the excess of alcohol, by steam-distillation of the acidified reaction mixture. These proved to be *m*-tolylacetonitrile (IV), which was identified by conversion into the beautifully crystalline amide, m. p. 141° (compare Radziszewski and Wispek, *Ber.*, 1885 ,**18**, 1281), *m*-xylene (V), identified by b. p. and analysis, and a little unchanged *m*-phenylenediacetonitrile. Considerable quantities of free hydrocyanic acid could also be detected.

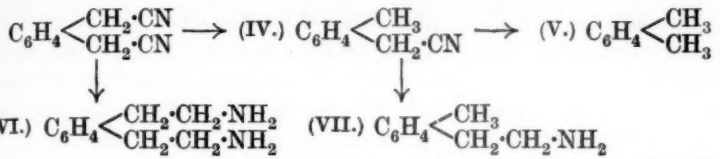
The basic products, after liberation from the acid solution by excess of sodium hydroxide, proved to be a mixture of *m*-phenylene-ββ′-diethylamine (VI), b. p. 162°/18 mm., formed in accordance with the observation of von Braun in a 10—15% yield, and a monoamine of b. p. 97—98°/15 mm., obtained in about 40% yield, which appeared to be identical with the substance $C_{10}H_{13}N$ described by von Braun as a secondary amine.

This monoamine gave a hydrochloride, which crystallised in large, glistening leaflets of m. p. 160°, a sulphur-yellow picrate, m. p. 174°, a benzoyl derivative, m. p. 72°, a phenylthiocarbamide, m. p. 86—87°, a platinum salt which, after blackening between 230° and 240°, melted with vigorous decomposition at 246°, and a quaternary methiodide, m. p. 237°. (The substance described by von Braun as a secondary amine had in almost every respect the same properties, *viz.*, b. p. 97—98°/16 mm., the hydrochloride, m. p. 160°, the picrate, m. p. 176°, the benzoyl derivative, m. p. 72°, the phenylthiocarbamide, m. p. 87°, the platinum salt, m. p. 232°, and the quaternary methiodide, m. p. 236°.)

The amine, however, prepared in this way, did not give analytical results corresponding to the composition $C_{10}H_{13}N$, but invariably showed a higher hydrogen content. It was at first thought that it had the composition $C_{10}H_{15}N$, but careful analyses of several samples, including one prepared from the recrystallised hydrochloride, clearly suggested the composition $C_9H_{13}N$.

On treating a solution of the base in dilute hydrochloric acid with sodium nitrite, a brisk evolution of nitrogen occurred and a pale yellow oil separated. This oil, which had a characteristic pungent and rather sweet odour, dissolved readily in ether and, after shaking with dilute sodium carbonate to remove nitrous acid, gave no response to the Liebermann test.

In view of these results and the nature of the non-basic products of the reaction, it seems quite clear that the normal reduction of *m*-phenylenediacetonitrile to the diamine (VI) is largely accompanied by the conversion of first one and then the other $-CH_2\cdot CN$ group into $-CH_3$ groups, the intermediate stage being itself reduced to a monoamine. The process is best made clear by the following scheme:



The monoamine described above, although evidently identical, except in its behaviour towards nitrous acid, with the monoamine (I) of von Braun, is in reality β-*m*-tolylethylamine (VII).

In order to establish the identity of the monoamine beyond question, β-*m*-tolylethylamine was prepared by the reduction of *m*-tolylacetonitrile (IV) with sodium and alcohol. Using approximately twice the theoretical quantity of reducing agent, a yield of about 50% of β-*m*-tolylethylamine was obtained, practically the whole of the rest of the nitrile being reduced to *m*-xylene.

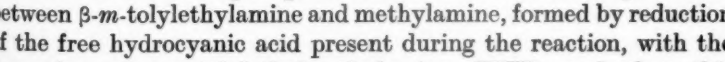
The amine had b. p. 216°/762 mm. and 98°/15 mm. and gave a hydrochloride, m. p. 160°, and a picrate, m. p. 174°, in accordance with the observations of Sommer (*Ber.*, 1900, **33**, 1079).

The benzoyl compound, phenylthiocarbamide, and quaternary methiodide also had the same melting points as the corresponding compounds, prepared from the specimen of monoamine which had been obtained by reducing *m*-phenylenediacetonitrile. There was no depression of the m. p. on mixing samples of these derivatives.

This reduction of the $-CH_2 \cdot CN$ group to $-CH_3$, although apparently of rare occurrence, is not unknown, and a few instances are recorded in the literature—for example, the reduction of cyanomethylbenziminazole to methylbenziminazole with sodium and alcohol (Bloch, *J. Soc. Chem. Ind.*, 1919, **38**, 118).

β-*m*-Tolylethylamine combines readily with piperonal, the condensation product crystallising well and melting at 53—54°. After being heated in a sealed tube with a slight excess of methyl iodide and then decomposed with aqueous alcohol, the latter yields β-m-*tolylethylmethylamine hydriodide*, m. p. 104°, from which the free base (VIII) was obtained, b. p. 88°/12 mm.

This base was prepared because of the very definite statement made by von Braun regarding the secondary nature of his monoamine. It was thought possible that interaction might occur between β-*m*-tolylethylamine and methylamine, formed by reduction of the free hydrocyanic acid present during the reaction, with the formation of β-*m*-tolylethylmethylamine (VIII), and that this secondary amine ($C_{10}H_{15}N$), in itself and in its derivatives, might closely resemble the primary amine ($C_9H_{13}N$).



This, however, was not found to be the case, since the secondary amine gave a hydrochloride extremely soluble in alcohol and most other solvents, which, when crystallised from chloroform–ligroin, had m. p. 134°. The picrate had m. p. 127°, whilst the benzoyl compound was an oil which could not be induced to crystallise.

No evidence of the formation of any secondary amine by the reduction of *m*-phenylenediacetonitrile was forthcoming, and since the properties of β-*m*-tolylethylamine and its derivatives agree in almost every respect with those of the monoamine described by von Braun, there seems little doubt that the two are identical.

As previously mentioned, von Braun, Karpf, and Garn found that the quaternary ammonium hydroxide of their base, on distillation, lost dimethylamine and water with the formation of an unsaturated hydrocarbon, $C_{10}H_{10}$ (II), which had b. p. 62—63°/18 mm. and added two atoms of bromine with the formation of a dibromide, m. p. 48°.

It was found that the quaternary methiodide of β-*m*-tolylethylamine, on boiling with methyl-alcoholic potash, lost trimethylamine (identified by means of the picrate and platinum salt), with the formation of *m*-methylstyrene (IX), b. p. 62°/18 mm., which by the addition of two atoms of bromine gave the corresponding dibromide (X), m. p. 47° (Müller, *Ber.*, 1887, **20**, 1216, found m. p. 45°).

$$C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3,HI \longrightarrow \text{(IX.) } C_6H_4Me{\cdot}CH{:}CH_2 \longrightarrow \text{(X.) } C_6H_4Me{\cdot}CHBr{\cdot}CH_2Br.$$

The hydrocarbon described by von Braun is stated to have an abnormally low density ($d^{19°}$ 0·900) as compared with " the isomeric hydrocarbons 3-methylindene (*d* 0·968) and Δ^1-dihydronaphthalene (*d* 0·997)," whilst it resembled a styrene in polymerising under the action of light. The density of *m*-methylstyrene was found to be 0·906 at 16° and its tendency to polymerise has been noted by previous workers (Müller, *loc. cit.*).

The saturated hydrocarbon (III) prepared by von Braun had the low density $d^{17·3°}$ 0·852 as compared with 1-methylhydrindene (*d* 0·966) and 1 : 2 : 3 : 4-tetrahydronaphthalene (*d* 0·968), whilst the refractive index was $n_D^{17°} = 1·497$.

The reduction of *m*-methylstyrene to *m*-tolylethane was not investigated, but it may be noted that the density of the latter is recorded by Wroblewski (*Annalen*, 1878, **192**, 198) as 0·869 at 20°. The refractive index of *m*-tolylethane has not apparently been measured, but that of the isomeric *p*-tolylethane is stated to have the value $n_D^{14°} = 1·494$ (Klages and Keil, *Ber.*, 1903, **36**, 1637).

Reduction of p-*Phenylenediacetonitrile.*

The reduction of *p*-phenylenediacetonitrile with sodium and alcohol was also investigated. In this case, the $-CH_2 \cdot CN$ groups are reduced to methyl groups even more readily than those in the *m*-isomeride, a yield of about 50% of β-*p*-tolylethylamine being obtained. The rest of the nitrile was almost wholly reduced to *p*-xylene, whilst no appreciable quantity of *p*-phenylene-ββ′-diethylamine was formed.

The identity of the monoamine was again established by reducing *p*-tolylacetonitrile, which yielded the same product.

β-*p*-Tolylethylamine has b. p. 94—95°/13 mm. and absorbs carbon dioxide rapidly from the air. It forms a sparingly soluble hydrochloride, m. p. 216° (compare Ciesielski, *Anzeiger Akad. Wiss. Krakau*, 1906, 270; *Centr.*, 1907, I, 1793). On treatment with nitrous acid, it passes into an alcohol, which has the same characteristic sweet odour as that derived from β-*m*-tolylethylamine. This β-p-*tolylethyl alcohol* boils at 112°/12 mm. and combines with *p*-nitrobenzoyl chloride, yielding an *ester* which crystallises well and melts at 91°.

The amine forms a *picrate*, m. p. 155°, a platinum salt, m. p. 234°, a *benzoyl* derivative, m. p. 89°, and a quaternary *methiodide*, m. p. 244°. With piperonal, it forms a beautifully crystalline condensation product, m. p. 107°, which, by treatment with methyl iodide in the manner already described, is converted into β-p-*tolylethylmethylamine hydriodide*, m. p. 149°. The free *base* obtained from this had b. p. 96°/12 mm. and yielded a readily soluble *hydrochloride*, m. p. 191°, a *picrate*, m. p. 135°, and an oily benzoyl compound.

The quaternary methiodide of the base, on boiling with methyl-alcoholic potash, was converted into *p*-methylstyrene, b. p. 59—60°/12 mm., which yielded a dibromide, m. p. 45—46° (compare Klages and Keil, *loc. cit.*).

No evidence of any ring formation was obtained during these experiments.

EXPERIMENTAL.

ωω′-*Dibromo*-m-*xylene.*—The bromination of *m*-xylene to the ωω′-dibromo-compound was studied under various conditions, but the best results were obtained by following the directions of Atkinson and Thorpe (J., 1907, **91**, 1696). In this method, *m*-xylene is treated with rather more than the theoretical quantity of bromine required for monobromination, and the mixture of mono- and di-bromoxylenes separated by fractional distillation.

m-Xylene (200 g.) was treated at 130°, under reflux, with dry

bromine (405 g.) during about 6 hours. The product was freed from hydrogen bromide by 2 days' standing over solid caustic soda in a vacuum desiccator. The bulk of the monobromoxylene passed over at 110—115°/20 mm., and when the temperature reached 125° the distillation was stopped and the residue in the flask, which solidified almost completely on cooling, was broken up on a Büchner funnel, washed with a little low-boiling ligroin, and recrystallised from acetone. Large, colourless prisms, m. p. 76°, were obtained. The yield of dibromo-compound is about 35%.

The ω-monobromoxylene was refractionated through a column, and the fraction 100—101°/14 mm. collected and used for the preparation of *m*-tolylacetonitrile (see later). The yield of monobromide is about 45% (Found: Br, 43·0. Calc., Br, 43·2%).

ωω'-*Dibromo*-p-*xylene*.—The bromination of *p*-xylene was carried out in the same manner as the above, using a quantity of bromine equal to twice the weight of the *p*-xylene taken. The reaction product solidified completely, and after pressing on a porous plate was extracted with ligroin (b. p. 40—50°) in a Soxhlet apparatus, which dissolved all the monobromide. The crude dibromo-compound crystallised from a small volume of warm chloroform in compact clusters of prisms, m. p. 143—144°.

The monobromo-compound, obtained by evaporation of the ligroin extract, after another crystallisation from the same solvent, separated in very long, colourless needles, m. p. 35·5°.

m-*Phenylenediacetonitrile*.—The conversion of the dibromoxylenes into the corresponding nitriles is usually attended by side-reactions leading to the formation of oily or amorphous by-products. These effects are minimised if the reaction is carried out as rapidly as possible, and the following method was found, in the case of dibromo-*m*-xylene, to give practically quantitative results.

A boiling solution of potassium cyanide (50 g.) in water (110 g.) and ethyl alcohol (350 c.c.) is rapidly stirred mechanically while finely powdered dibromo-*m*-xylene (88 g.) is added as rapidly as the violence of the reaction will permit. The hot solution is filtered at once from traces of brown, amorphous material. A litre of water is then added and the nitrile extracted with ether, dried, and distilled. The nitrile boiled at 230—231°/20 mm. and solidified, on cooling, to a snow-like mass of needles, m. p. 27°. Yield, 47 g.

m-*Tolylacetonitrile*.—Monobromo-*m*-xylene (128 g.) was treated with potassium cyanide (49 g.) dissolved in a mixture of water (120 g.) and alcohol (400 c.c.) in exactly the same manner as the above. The nitrile (yield about 85%) boiled at 245—247°/745 mm. with slight decomposition (compare Radziszewski and Wispek,

loc. cit.) and was better distilled under reduced pressure; it then had b. p. 133°/15 mm.

p-*Phenylenediacetonitrile.*—The nitrile was prepared in the same manner as the meta-isomeride, the same quantities and conditions being used. The maximum possible yield, however, seems to be about 70%. The remainder of the bromo-derivative is converted into a bright yellow, infusible, amorphous, highly insoluble product, which does not appear to contain any nitrogen or halogen and was not further investigated. The nitrile separates from alcohol in colourless prisms, m. p. 96°.

p-*Tolylacetonitrile.*—This nitrile was obtained from monobromo-*p*-xylene by the usual method. It was found necessary in this case to boil the reaction mixture for a short time to complete the conversion. The nitrile has b. p. 135°/14 mm. and solidifies in ice to a white mass which melts at 17°.

Reduction of m-*Phenylenediacetonitrile.*—Sodium (36·8 g.) in the form of small chips was placed in a 3-litre flask, closed with a cork through which passed an air condenser about 4 feet in length and 1½ inches in diameter. This was itself fitted at the top with a water-condenser. (In some experiments, the sodium was previously granulated under toluene, but this did not appear to affect the yield materially.)

A nearly boiling solution of *m*-phenylenediacetonitrile (14·6 g.) in absolute alcohol (550 g.) was then rapidly added. When the extremely violent reaction had subsided, a solution of 90 g. of concentrated sulphuric acid in 300 c.c. of water was added and the mixture distilled in steam. The acid solution was filtered from traces of a brown, sticky by-product, and, if necessary, extracted with ether. It was then rendered alkaline with caustic soda (30 g.) and thoroughly extracted with ether. After the ethereal solution had been dried with anhydrous magnesium sulphate and the ether removed, 8 g. of a pale yellow oil were obtained, from which 5—6 g. of b. p. 97—98°/15 mm. or 101—102°/18 mm. were isolated (Found: C, 80·1, 80·2; H, 9·8, 9·7; N, 10·25. $C_9H_{13}N$ requires C, 80·0; H, 9·6; N, 10·4%).

The combined aqueous-alcoholic steam distillates from three such experiments were distilled through a column until about three-quarters of the alcohol had been removed. Water was then added to the residue, and the insoluble material extracted with ether. After removal of the ether, about 15 g. of non-basic products were obtained, and from these, by careful fractionation, 8—9 g. of a liquid, b. p. 138—141°/758 mm., which had a xylene-like odour and burned with a smoky flame (Found: C, 90·1; H, 9·3. Calc. for C_8H_{10}: C, 90·6; H, 9·4%).

From the residue about 4—5 g. of a liquid, b. p. 138—140°/18 mm., were obtained which, after shaking with dilute hydrogen peroxide and standing over-night, were converted into a crystalline mass. Recrystallised from hot water, the substance formed colourless leaflets, m. p. 141—142°, and analysis left no doubt that it was identical with *m*-tolylacetamide (compare Radziszewski and Wispek, *loc. cit.*) (Found : N, 9·6. Calc. for $C_9H_{11}ON$: N, 9·7%).

The amine, b. p. 97—98°/15 mm., described above, absorbed carbon dioxide readily from the air, with the formation of a solid carbonate.

The hydrochloride of the base was readily obtained by passing dry hydrogen chloride into its alcoholic solution. It separated in large, transparent laminæ, m. p. 160° (Found : C, 63·4; H, 8·35. $C_9H_{13}N,HCl$ requires C, 63·0; H, 8·2%).

The picrate, obtained by adding an alcoholic solution of the base to a saturated alcoholic solution of picric acid, formed sulphur-yellow needles, m. p. 174° (176° corr.) (compare Sommer, *loc. cit.*) (Found : N, 15·4. Calc., N, 15·4%).

The platinum salt, which separated in small, orange-brown needles on mixing warm solutions of the hydrochloride of the base and chloroplatinic acid, blackened between 230° and 240° and melted with vigorous decomposition at 246° (von Braun found m. p. 232° for this substance) (Found : Pt, 28·85. Calc. for $2C_9H_{13}N,H_2PtCl_6$: Pt, 28·7%).

The benzoyl derivative was best obtained by mixing 1 g. of the hydrochloride with 0·9 g. of benzoyl chloride and adding 15 c.c. of a 5% solution of sodium hydroxide. The sticky, white mass gradually solidified; recrystallised either from a very small volume of alcohol or from alcohol–ligroin, it formed colourless prisms, m. p. 72°.

The phenylthiocarbamide was obtained by boiling a solution of equal weights of the base and of phenylthiocarbimide in alcohol for about 10 minutes and adding ligroin; the thiocarbamide separated in colourless needles, which were recrystallised from a little warm alcohol and then had m. p. 86—87°.

The quaternary methiodide was easily prepared by shaking a mixture of the base (4·5 g.) with methyl iodide (20 g.) and 75 c.c. of a 5% solution of sodium hydroxide. Considerable heat was developed and the quaternary salt was deposited in white crusts. It crystallised from alcohol, in which it was only very moderately soluble in the cold, in colourless prisms, m. p. 237°.

Reduction of m-*Tolylacetonitrile.*—This reduction was carried out in the same apparatus and by the same method as that of the dinitrile already described. Thirty g. of sodium were used to reduce a solution of 15 g. of *m*-tolylacetonitrile in 450 g. of absolute alcohol.

The reaction products were worked up in the same manner, giving a yield of about 7 g. of β-*m*-tolylethylamine, b. p. 98°/15 mm. or 112°/25 mm., and about 5 g. of *m*-xylene (Found : C, 79·9; H, 9·8; N, 10·2. Calc. for $C_9H_{13}N$: C, 80·0; H, 9·6; N, 10·4%).

Condensation of β-m-*Tolylethylamine with Piperonal.*—A mixture of the base (10 g.) with piperonal (11 g.) was warmed on the water-bath for ½ hour. The product, which solidified on cooling, crystallised from about 100 c.c. of hot alcohol in yellowish-white leaflets, m. p. 54° (Found : C, 76·5; H, 6·6. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4%).

β-m-*Tolylethylmethylamine.*—The carefully dried piperonal compound (15 g.) was mixed with an equal weight of methyl iodide and heated for 6 hours in a sealed tube at 100°. The excess of methyl iodide was boiled off and the residue dissolved in about 75 c.c. of 95% alcohol. On diluting the solution with three times its volume of ether, the *hydriodide* of the secondary base was precipitated in needles which, after being washed with ether, were faintly yellow and had m. p. 107° (Found : I, 45·5. $C_{10}H_{15}N,HI$ requires I, 45·8%).

The free *base*, obtained by dissolving the hydriodide in an excess of 10% sodium hydroxide and extracting with ether, had b. p. 88—89°/12 mm. (Found : C, 80·5; H, 9·8; N, 9·6. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1; N, 9·4%).

The *hydrochloride* was best prepared by passing dry hydrogen chloride into a solution of the base in chloroform and adding ligroin, when it separated in greasy-looking leaflets, m. p. 134°. It is very soluble in alcohol and water and is usually obtained from these solvents, on evaporation, as an oil.

The *picrate* separated in orange needles, on mixing strong alcoholic solutions of the base and picric acid, and had m. p. 126—127° (Found : N, 14·7. $C_{10}H_{15}N,C_6H_3O_7N_3$ requires N, 14·8%).

The benzoyl derivative was obtained as a viscous oil on mixing the base with benzoyl chloride and dilute caustic soda. It showed no signs of crystallisation even on cooling in a freezing mixture.

m-*Methylstyrene.*—The quaternary methiodide of β-*m*-tolylethylamine (9 g.) was heated on the water-bath with 25% methyl-alcoholic potash (20 g.) in a small flask fitted with a reflux condenser closed with a cork, through which passed a delivery tube dipping into dilute hydrochloric acid. After 1 hour, when the decomposition appeared to be complete, water was added, the insoluble oily layer extracted with ether, and the ethereal solution washed with very dilute hydrochloric acid, dried, and distilled. The hydrocarbon obtained (3—4 g.) had b. p. 61—62°/18 mm. (Found : C, 91·3; H, 8·5. C_9H_{10} requires C, 91·5; H, 8·5%).

From the hydrochloric acid solution through which the gaseous products of the decomposition had been passed, trimethylamine hydrochloride, m. p. 280° (decomp.) (compare Wagner, *Z. Kryst. Min.*, 1906, **43**, 167) was obtained. The chloroplatinate prepared therefrom formed brown scales, m. p. 242—243° (compare Willstätter, *Ber.*, 1895, **28**, 3287), and the picrate formed golden-yellow prisms, m. p. 216°, from alcohol (compare Delépine, *Ann. Chim.*, 1896, **8**, 452). Conclusive evidence was thus obtained that trimethylamine, and not dimethylamine, is eliminated during this decomposition.

From the density and the observed value of the refractive index ($n_D^{19°}$ 1·54029), von Braun calculated the molecular refraction of his hydrocarbon, assuming, of course, the composition (II), and obtained the value $[R_L]_D$ 45·33, whilst that calculated for the composition $C_{10}H_{10}$ was 42·11. He attributes this large exaltation of 3·2 units to the presence of the meta-ring structure. If, however, the molecular refraction is calculated from the same data, but assuming the composition C_9H_{10}, the value 41·15 is obtained, whilst that predicted theoretically (using Conrady's constants) is 39·70—giving an exaltation of only 1·4 units. This exaltation is of the order to be expected in a substance of the structure (IX) (EM_a for the isomeric β-methylstyrene is 1·01 units).

αβ-*Dibromo*-α-m-*tolylethane*.—*m*-Methylstyrene (1·5 g.) dissolved in 10 c.c. of carbon disulphide was cooled in ice and gradually treated with a solution of 2·1 g. of bromine in 10 c.c. of carbon disulphide. After evaporation of the solvent, the crystalline residue was dissolved in a small volume of warm alcohol, from which it separated in well-formed, large prisms, m. p. 47° (compare Müller, *loc. cit.*) (Found: C, 39·2; H, 3·8; Br, 57·5. Calc., C, 38·8; H, 3·6; Br, 57·6%).

Reduction of p-*Phenylenediacetonitrile and* p-*Tolylacetonitrile*.—The reduction of these two substances was carried out in precisely the same manner as that of the meta-isomerides.

The same product, *viz.*, β-*p*-tolylethylamine, was obtained from both, as well as recognisable quantities of *p*-xylene.

The β-*p*-tolylethylamine, obtained in about 50% yield by reducing the dinitrile and in nearly 60% yield from the mononitrile, had b. p. 94—95°/13 mm. (Found: C, 79·6; H, 9·7; N, 10·7. $C_9H_{13}N$ requires C, 80·0; H, 9·6; N, 10·4%).

The *hydrochloride*, which is quite sparingly soluble in water and nearly insoluble in cold alcohol, crystallises in large plates, m. p. 216° (Found: C, 63·4; H, 8·25. $C_9H_{13}N,HCl$ requires C, 63·0; H, 8·2%). The *picrate* forms pale yellow needles, m. p. 155°, from alcohol (Found: N, 15·7. $C_9H_{13}N,C_6H_3O_7N_3$ requires N, 15·4%).

The *benzoyl* derivative is very readily soluble in most solvents, but can be crystallised from a small volume of alcohol in colourless prisms, m. p. 89° (Found : C, 80·5; H, 7·1. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%). The quaternary *methiodide* has m. p. 244° and is sparingly soluble in cold alcohol.

On treatment with an excess of an acid solution of sodium nitrite, the amine was converted into β-p-*tolylethyl alcohol*, which had b. p. 112°/12 mm., and when warmed with *p*-nitrobenzoyl chloride was converted into a solid ester, which separated from alcohol in small, colourless needles, m. p. 91° (Found : C, 67·0; H, 5·45. $C_{16}H_{15}O_4N$ requires C, 67·3; H, 5·3%).

With piperonal, the amine formed a beautifully crystalline condensation product, m. p. 107°, only sparingly soluble even in hot alcohol (Found : C, 76·7; H, 6·55. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4%).

β-p-*Tolylethylmethylamine.*—The piperonal compound was heated in a sealed tube with an excess of methyl iodide in the manner previously described. The hydriodide of the secondary base, obtained on decomposition of the product with aqueous alcohol, had m. p. 149°. From this the free base was obtained, b. p. 96°/12 mm. (Found : C, 80·4; H, 10·25; N, 9·4. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1; N, 9·4%).

The hydrochloride is readily soluble in most solvents, but does not exhibit the extreme solubility of the meta-isomeride. It separates from cold alcohol in plates, m. p. 191°. The picrate forms deep orange prisms, m. p. 135°, from alcohol (Found : N, 14·7. $C_{16}H_{18}O_7N_4$ requires N, 14·8%).

p-*Methylstyrene.*—β-*p*-Tolylethylamine hydriodide is readily converted into the hydrocarbon by boiling with 25% methyl-alcoholic potash.

p-Methylstyrene has b. p. 59—60°/12 mm. and does not appear to undergo polymerisation as rapidly as the meta-isomeride (Found : C, 91·2; H, 8·7. C_9H_{10} requires C, 91·5; H, 8·5%).

Treated in carbon disulphide solution with the equivalent of two atoms of bromine, it is converted into αβ-dibromo-α-*p*-tolylethane, m. p. 46° (compare Klages and Keil, *loc. cit.*) (Found : Br, 57·15. Calc., Br, 57·6%).

My thanks are due to the Ramsay Memorial Trustees for a Fellowship during the tenure of which this work was carried out. I also wish to thank Professor W. H. Perkin for his interest and advice and Dr. R. D. Haworth for some valuable suggestions.

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LXVIII.—*The Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part II. Tellurium Dioxide.*

By Edmund Brydges Rudhall Prideaux and John O'Neil Millott.

The action of hydrofluoric acid upon tellurium dioxide was studied by Metzner (*Ann. Chim. Phys.*, 1898, **15**, 203). The oxide dissolved in the 43—55% acid. On cooling to about −50°, crystals were obtained which contained 53% of hydrogen fluoride. The solutions crystallised on evaporation to small bulk, and successive crops corresponded best with the formulæ $2TeF_4,3TeO_2,6H_2O$ and $TeF_4,TeO_2,2H_2O$, the analyses of the latter compound being the more concordant and agreeing better with the formula assigned. The mother-liquor from this preparation was treated with hydrofluoric acid "pur." (from potassium hydrogen fluoride) and cooled to − 70°. It then formed transparent crystals containing 3·8 atoms of fluorine for each atom of tellurium. This compound was regarded as TeF_4. The author remarks that its preparation in the pure state would require very concentrated acid. We have used anhydrous hydrogen fluoride throughout our investigation, but have not so far observed the crystallisation of this compound. We have, however, confined our experiments mainly to the preparation of that fluoride which is obtained at the ordinary temperature.

Experimental.

Tellurium, supplied by the courtesy of the Baltimore Copper Company, was dissolved in nitric acid, and the solution evaporated to dryness. The product was slightly green owing to the presence of copper, which was removed by fusion with sodium carbonate and extraction with water followed by filtration. The solution was made faintly acid with nitric acid, and the precipitated tellurous acid was filtered off, dried at 100°, heated to its melting point, and powdered.

The anhydrous hydrogen fluoride, prepared as already described (Part I, this vol., p. 167), was passed over the dioxide in a platinum boat or crucible, contained in a copper tube or copper-plated cylinder, respectively. A colourless liquid was produced and a white solid, consisting apparently of unchanged tellurium dioxide, remained. This dissolved completely in excess of hydrogen fluoride. The liquid was exposed for several days in a vacuous desiccator, covered inside with ceresin and containing calcium chloride and solid sodium hydroxide. It became slightly more viscous and remained clear.

On cooling to — 70°, it became very viscous, but no crystals appeared on stirring and rubbing. After standing for another day, it suddenly set to a mass of white crystals. This is the product A mentioned below.

The preparation was repeated with slight variations. The hydrogen fluoride vapour was passed until some of the oxide had dissolved and some had been converted into silky crystals, which adhered firmly to the crucible. The liquid was then decanted into a platinum capsule. The undissolved dioxide and the silky crystals were dissolved in more liquid hydrogen fluoride which had been condensed in a platinum bottle. Both solutions were placed at once in the desiccator described above, which was then evacuated. After about 2 days, a mass of white nodules of radiating crystalline structure separated from each solution. This is sample B.

These crystals were kept, in a desiccator, unchanged for days at atmospheric pressure. When the desiccator was evacuated over phosphorus pentoxide for a night, 0·5525 g. of the substance lost only 3 mg. But when this treatment was continued for several days (sample B1) or when the compound was kept over alkali in a desiccator for months (sample A1), the composition changed in the manner indicated by the analyses given below.

Analysis.—Since the accurate gravimetric estimation of fluoride in the presence of tellurite is difficult (Metzner, *loc. cit.*), we have devised a method of estimating it as hydrogen fluoride after hydrolysis. When a solution of tellurous acid in dilute hydrofluoric acid is titrated with alkali in the presence of *p*-nitrophenol, precipitation of tellurous acid begins at once and continues until the indicator turns yellow. When tellurous acid is suspended in water, a single drop of alkali produces this colour change. Therefore, on account of its sparing solubility, the tellurous acid gives a solution of $[H^+] = 1 \times 10^{-5}$ or even less. A weighed amount of hydrofluoric acid, when titrated in the presence of tellurous acid, required exactly the same amount of alkali as the same weight of hydrofluoric acid when titrated alone. Tellurous acid, therefore, can be disregarded at the *p*-nitrophenol end-point. Although this titration gives concordant figures, these do not, as shown in Part I (*loc. cit.*), correspond with the absolute amount of hydrofluoric acid present until multiplied by a factor 1·03.

The samples were analysed after being crushed and rubbed between filter-paper.

Tellurium was estimated as usual after precipitation by sulphur dioxide from a hydrochloric acid solution.*

* In the volumetric analysis, the titrated liquid was proved to be free from tellurium, and the precipitate free from fluoride.

Sample A: 0·273 g. required 28·57 c.c. of *N*/10-alkali and gave 0·1805 g. of tellurium. Sample B: 0·9005 g. required 92·3 c.c. of *N*/10-alkali, and 0·382 g. gave 0·2545 g. of tellurium.

	A.	B.	A1.	B1.
% Te	66·1	66·6	68·7	70·2
% F	20·4	20·0	18·6	18·9

TeF_4,TeO_2,H_2O requires Te, 66·8; F, 20·0%. $TeF_4,TeO_2,2H_2O$ requires Te, 63·8; F, 19·1%.

The use of anhydrous hydrogen fluoride therefore leads to a compound different from either of those prepared by Metzner. In the presence of more water, more hydrated compounds would doubtless be formed. Since the only water present in our experiments was that formed in the reaction, it is evident that at least one molecule is thus produced and evaporates in the desiccator. The other molecule, if it is really eliminated, is held as water of crystallisation but has only a low vapour pressure.

We regard this compound as the least hydrated which it is possible to prepare from the dioxide and hydrogen fluoride with subsequent evaporation. It is not at present possible to decide between the formulæ TeF_4,TeO_2,H_2O, $2TeOF_2,H_2O$, and $TeOF_2,TeO_2,2HF$. In material kept in the desiccator after a long time (A1), or in a vacuum over phosphorus pentoxide (B1), the percentage of tellurium increases considerably, whilst the percentage of fluorine diminishes only slightly. These results suggest that, under the conditions employed, more water is lost than hydrogen fluoride, so that the compound behaves rather as a hydrate than as a fluoride.

One of us wishes to repeat his grateful acknowledgment to the Royal Society of a grant which has supplied some of the apparatus required for this and the preceding research. The other (J. O'N. M.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 9th*, 1925.]

LXIX.—*The Action of Alcoholic Potassium Hydroxide upon Chloronitrobenzene.*

By DONALD HENRY RICHARDSON.

HEUMANN (*Ber.*, 1872, **5**, 910) obtained *pp'*-dichloroazoxybenzene by boiling *p*-chloronitrobenzene with alcoholic potash. Willgerodt (*Ber.*, 1879, **12**, 767) showed that *p*-nitrophenetole and *p*-nitrophenol also are products of the reaction, and later (*Ber.*, 1882, **15**, 1002) found that dilution of the alcohol with water diminishes the form-

ation of dichloroazoxybenzene. Blom (*Helv. Chim. Acta*, 1921, **4**, 297) studied the kinetics of the reaction and found that by using aqueous alcohol at 70° no dichloroazoxybenzene is formed.

In an investigation with the object of discovering the conditions under which the maximum yield of nitrophenetole free from chloronitrobenzene could be most easily obtained, it was found that the formation of dichloroazoxybenzene could be avoided without dilution of the alcohol if the temperature was reduced to 60°, and the alkali strength to 0·2 normal. Excellent results having been obtained on the small scale, some large-scale trials were made in which 362 lb. of chloronitrobenzene were heated at 60° with 145 gallons of 0·2*N*-95% alcoholic soda, the alkali strength being maintained by the addition of the estimated amount of the powdered solid at frequent intervals. At the first attempt, in spite of considerable accidental loss, the yield amounted to 277 lb. of nitrophenetole, free from chloronitrobenzene, and containing only 3·4% of dichloroazoxybenzene, but in all subsequent experiments at least 17% of the theoretical amount of azoxy-compound was formed. It was not realised at the time that the alcohol used in the first experiment had been specially purified for pharmaceutical purposes, and the systematic investigation to be described was undertaken to discover the cause of the failure of the process.

The conclusions are as follows:

1. The presence of as much as 0·1% of acetaldehyde in the alcohol causes considerable reduction of the chloronitrobenzene, and the larger the percentage of acetaldehyde, the greater is the yield of dichloroazoxybenzene.

2. The formation of dichloroazoxybenzene may be avoided without dilution of the alcohol with water if chloronitrobenzene is heated for 140 hours at 60° in a 0·5*N*-solution of caustic potash in 95% ethyl alcohol free from acetaldehyde.

3. Under these conditions, 92% of the theoretical yield of pure *p*-nitrophenetole, 90% of *o*-nitrophenetole, and 96% of *p*-nitroanisole (using methyl alcohol) may be obtained, nitrophenol being the only by-product.

4. As the temperature or alkali concentration is raised, dichloroazoxybenzene is formed in rapidly increasing amount, even if the alcohol is free from acetaldehyde.

5. Under conditions resulting in the formation of a considerable amount of dichloroazoxybenzene, *p*-chloroaniline is also formed in appreciable quantity.

6. Although the reducing action of alcoholic alkali is decreased by dilution of the alcohol with water (Willgerodt, *loc. cit.*), this diminishes the rate of conversion of chloronitrobenzene into nitrophenetole.

7. Nitrophenol is always a by-product when chloronitrobenzene is heated with alcoholic alkali solution, and the yield is increased as the temperature and the strength of alkali are raised, but is not greatly affected by dilution of the alcohol with water.

Experimental.

Five series of experiments were carried out, in each of which only one factor was subjected to variation. Pure chloronitrobenzene was heated at a constant temperature in a large excess of a standard solution of potash in alcohol of known strength. After a noted time, the solution was nearly neutralised with sulphuric acid, the alcohol distilled off, and the nitrophenetole isolated by blowing steam through the residue. Its weight and melting point were determined after filtering off and drying over calcium chloride in a vacuum desiccator. Nitrophenetole was appreciably volatile in alcohol vapour, and was estimated in the alcohol recovered by evaporating a known volume in a vacuum desiccator at laboratory temperature, and weighing the residue. Ether extraction of the filtered steam distillate showed that nitrophenetole was soluble in water at 15° to the extent of 0·11 g. per litre. The insoluble dichloroazoxybenzene was filtered off from the residual liquors, washed, dried, and weighed without further purification. After evaporation to smaller bulk, the filtrate and washings were acidified with sulphuric acid and the *p*-nitrophenol was extracted with ether.

The conditions in each series of experiments are described below, and the yields given in tabular form.

Series 1.—*Variation in strength of alkali.* A solution of caustic potash in 95% alcohol was standardised and diluted with the calculated volume of alcohol so that 250 c.c. each of a 0·1, 0·2, 0·3, 0·4, and 0·5 *N*-solution of potash were obtained. Exactly 4 g. of pure chloronitrobenzene were dissolved in each solution, and all were heated together in a thermostat at 60°. After 187 hours' heating, 5 c.c. of each solution were titrated with *N*/10-sulphuric acid to determine the final concentration of the potash, and the reaction products analysed as previously described. The results are tabulated below :

Experiment.	1.	2.	3.	4.	5.
Strength of KOH (*N*) : initial ...	0·1	0·2	0·3	0·4	0·5
„ „ „ final ...	0·013	0·064	0·165	0·226	0·405
Wt. of nitrophenetole (g.)	3·19	3·61	3·24	2·86	1·91
M. p. of nitrophenetole	46°	57°	57°	57°	57°
Wt. of dichloroazoxybenzene (g.)	0·02	0·10	0·37	0·70	0·92
Wt. of *p*-nitrophenol (g.)	0·04	0·09	0·13	0·28	0·50
% Theoretical yield :					
Nitrophenetole.....	75·3	85·1	76·4	67·5	44·8
Dichloroazoxybenzene	0·6	2·9	10·9	20·6	27·1
Nitrophenol	1·1	2·6	3·7	7·9	14·2
Total	77·0	90·6	91·0	96·0	86·1

The low melting point of the nitrophenetole obtained in experiment 1 showed that some unchanged chloronitrobenzene remained, as would be expected in view of the small final concentration of the potash in this case. A considerable amount of tarry matter was noted during the extraction of the nitrophenol in experiment 5, and a smaller amount in experiment 4. It was not found possible to account for the remainder of the yield at this point.

The results indicated that an increase in the concentration of alkali causes a greater production of both dichloroazoxybenzene and nitrophenol, this being most marked in the case of the azoxy-compound.

Series 2.—*Variation in strength of alcohol.* Five 0·5*N*-potash solutions were prepared, one in absolute alcohol, and the other four in 95% alcohol diluted with noted volumes of water to a total of 250 c.c. each. The five solutions were heated in a constant-temperature water-bath at 60° for 24 hours, after which 4 g. of chloronitrobenzene were dissolved in each and the heating was continued for 187 hours.

The products were analysed with the following results:

Experiment.	6.	7.	8.	9.	10.
Strength of alcohol (%)	100	87	80	70	60
Wt. of nitrophenetole (g.)	3·834	3·497	3·453	3·348	3·019
M. p. of nitrophenetole	57°	57°	57°	56°	56°
Wt. of dichloroazoxybenzene (g.)	0·025	0·129	0·157	0·071	0·106
Wt. of nitrophenol (g.)	Lost by accident.	0·484	0·488	0·469	0·455
% Theoretical yield:					
Nitrophenetole	90·4	82·5	81·4	78·9	71·2
Dichloroazoxybenzene	0·7	3·8	4·6	2·1	3·1
Nitrophenol	?	13·7	13·8	13·3	12·9
Total	(91·1)	100·0	99·8	94·3	87·2

The melting point of the nitrophenetole obtained in experiments 9 and 10 showed that a small amount of chloronitrobenzene remained unchanged, indicating that dilution of the alcohol retards the rate of conversion of chloronitrobenzene into nitrophenetole. The most remarkable result was the very small yield of dichloroazoxybenzene in all five experiments, in spite of a concentration of potash equal to that in experiment 5, in which a 27% yield of the azoxy-compound was obtained.

The use of absolute alcohol having resulted in the smallest production of dichloroazoxybenzene, it seemed probable that some impurity in the alcohol was the cause of the formation of the azoxy-compound. Since the chloronitrobenzene is reduced to dichloroazoxybenzene, acetaldehyde would be the most likely impurity to cause this reduction. The preliminary 24 hours' heating of the alcoholic potash before the introduction of the chloronitrobenzene would have at least partly resinified the aldehyde, so accounting

for the small yield of dichloroazoxybenzene in these five experiments. It was noted that a yellow colour developed in the alcoholic potash solutions during the preliminary heating, indicating the formation of aldehyde-resin.

Series 3.—*Effect of acetaldehyde upon the production of dichloroazoxybenzene.* To determine the effect of acetaldehyde upon chloronitrobenzene in alcoholic potash solution, a third series of five experiments was commenced, using 250 c.c. of 0·5 *N*-alkali in 95% alcohol. The chloronitrobenzene was added before heating in experiment 11, but after 66 hours' preliminary heating in experiment 12, while 25 c.c. of hydrogen peroxide solution were added in experiment 13. Methylated spirit known to contain acetaldehyde was used in experiment 14, and 10 c.c. of acetaldehyde were added to the alcohol in experiment 15, in both cases the chloronitrobenzene being added before heating was commenced. The five solutions were heated simultaneously for 235 hours at 60°, and gave the following yields on analysis :

Experiment.	11.	12.	13.	14.	15.
Wt. of nitrophenetole (g.)	3·69	3·77	3·58	2·13	0·82
Wt. of dichloroazoxybenzene (g.)	0·04	0·02	0·015	0·315	2·29*
Wt. of nitrophenol (g.)	0·43	0·41	0·52	0·68†	0·67†
% Theoretical yield :					
Nitrophenetole.....	87·0	88·9	84·4	50·2	19·2
Dichloroazoxybenzene	1·2	0·6	0·5	9·3	67·6*
Nitrophenol	12·2	11·5	14·7	19·5†	19·0†
Total	100·4	101·0	99·6	79·0	105·8

* Includes aldehyde-resin. † Includes tar.

The very large yield of dichloroazoxybenzene in the presence of acetaldehyde left little cause for doubt that the latter plays an important part in the reduction of the chloronitrobenzene. It was resolved to test this conclusion by heating chloronitrobenzene with alcoholic potash containing known small quantities of acetaldehyde.

Acetaldehyde was eliminated from ethyl alcohol as completely as possible by refluxing with 0·2% of *m*-phenylenediamine hydrochloride for 12 hours, after which the alcohol was distilled off through a fractionating column, the first 100 c.c. of the distillate being rejected. The product gave no colour on standing with Schiff's reagent, and remained practically colourless after heating for 24 hours with 0·5*N*-potash at 60°.

A standard solution of acetaldehyde was prepared by dissolving about 10 c.c. of freshly distilled acetaldehyde (b. p. 21°) in 100 c.c. of aldehyde-free alcohol and estimating its strength by the sodium sulphite method.

Series 4.—*Effect of variation in concentration of aldehyde.* Three solutions were prepared containing measured volumes of the standard acetaldehyde solution diluted to 250 c.c. with aldehyde-free

alcohol in which was dissolved sufficient potash to give 250 c.c. of a 0·5*N*-solution. Four g. of chloronitrobenzene were dissolved in each, and all were heated simultaneously with a blank experiment, using the same aldehyde-free alcohol, for 160 hours at 60°. The following table gives the yields in the four experiments :

Experiment.	16.	17.	18.	19.
Strength of acetaldehyde (%)	0·0	0·14	0·2	0·67
Wt. of nitrophenetole (g.)	3·902	3·434	2·685	1·121
Wt. of dichloroazoxybenzene (g.) ...	Nil	0·317	0·536	2·178†
Wt. of nitrophenol (g.)	0·276	0·210	0·405*	0·468*
% Theoretical yield :				
Nitrophenetole	92·0	81·0	63·3	26·4
Dichloroazoxybenzene	0·0	9·3	15·8	64·2†
Nitrophenol	7·8	5·9	11·5*	13·3*
Total	99·8	96·2	90·6	103·9

* Includes tar. † Contained aldehyde-resin.

From these results, it is evident that the complete elimination of acetaldehyde from the reaction mixture prevents the formation of dichloroazoxybenzene, under the conditions obtaining in these experiments. As little as 0·1% of acetaldehyde appears to be capable of causing a considerable amount of reduction of the chloronitrobenzene, and an increase in the concentration of the aldehyde, within the limits investigated, causes a corresponding increase in the formation of dichloroazoxybenzene.

Experiments were now made to determine whether, with the use of aldehyde-free alcohol, the temperature and the alkali concentration could be increased without the formation of dichloroazoxybenzene. It had been noted that whenever the latter appeared in the reaction product in any quantity, the total yields of nitrophenetole, dichloroazoxybenzene, and nitrophenol did not account for the whole of the chloronitrobenzene employed. It was thought possible that a small amount of the latter might have become completely reduced to *p*-chloroaniline.

To investigate this possibility, the solutions obtained in the following series of experiments were acidified with dilute sulphuric acid before distilling off the alcohol. After steam distillation of the nitrophenetole and filtration of the dichloroazoxybenzene, the acid filtrate was made alkaline and distilled to a small volume. The distillate was extracted with ether, and the residue after its evaporation weighed.

The residue melted at 66°, was soluble in dilute acids and reprecipitated by alkali, and could be diazotised and coupled with β-naphthol to give a red dye. It was acetylated with acetyl chloride, and the product melted at 171—173°. After recrystallisation from dilute alcohol, it melted sharply at 177°. These facts indicated that the residue was *p*-chloroaniline.

Series 5.—*Effect of higher temperature, and greater concentration of alkali, on the reaction of chloronitrobenzene with aldehyde-free alcoholic potash.* Five solutions of potash in 250 c.c. of aldehyde-free alcohol were prepared so that two contained 0·5*N*-alkali, and the other three 1·0, 1·5, and 2·0 *N*-alkali, respectively. In each were dissolved 4 g. of chloronitrobenzene, and, whilst one of the 0·5 *N*-solutions was refluxed for 24 hours, the other four were heated for 140 hours at 60°.

The yields of nitrophenetole, nitrophenol, dichloroazoxybenzene, and chloroaniline in each of the five experiments were estimated as described above, with the following results:

Experiment.	20.	21.	22.	23.	24.
Strength of potash (*N*)	0·5	0·5	1·0	1·5	2·0
Wt. of nitrophenetole (g.)	1·241	3·800	2·134	0·778	0·328
Wt. of nitrophenol (g.)	0·553	0·279	0·434	0·364	0·304
Wt. of dichloroazoxybenzene (g.)	1·526	Nil	0·988	2·243	2·372
Wt. of *p*-chloroaniline (g.)	0·205	Nil	0·338	0·293	0·572
% Theoretical yield:					
Nitrophenetole	29·3	89·6	50·3	18·4	7·7
Dichloroazoxybenzene	45·0	0·0	29·1	66·2	70·0
Chloroaniline	6·3	0·0	10·4	9·1	17·7
Nitrophenol	15·7	7·9	12·3	10·3	8·6
Total	96·3	97·5	102·1	104·0	104·0
	Refluxed.		The dichloroazoxybenzene was very impure.		

These results proved conclusively that the absence of aldehyde from the alcohol does not preclude the formation of dichloroazoxybenzene under all conditions. They confirm the conclusion that higher temperature and higher concentration of alkali favour the reduction of the chloronitrobenzene, an appreciable quantity of which becomes completely reduced to *p*-chloroaniline whenever dichloroazoxybenzene is formed to any extent.

In order to determine the minimum time required for the conversion of chloronitrobenzene into nitrophenetole under the conditions giving the maximum yield, 63 g. of chloronitrobenzene in 2 litres of 0·5*N*-95% aldehyde-free alcoholic potash were heated at 60°, whilst 5 c.c. of the solution were titrated at intervals with *N*/10-acid, and the melting point of the precipitated chloronitrobenzene–nitrophenetole mixture was determined.

Experiment 25.

Time (hours).	*N*/10-H_2SO_4 (c.c.) for 5 c.c.	Strength of KOH (*N*).	Equivs. of KOH neutralised.	M. p. of ppted. product.
0	25	0·5	0·0	83°
28½	18·45	0·369	0·655	49—51
50	16·85	0·337	0·815	54—55
78½	15·75	0·315	0·925	55—56
142	15·0	0·300	1·0	56—57

After 142 hours, the whole solution was neutralised with dilute sulphuric acid, and the alcohol distilled off on the water-bath. The residue of nitrophenetole was well washed with dilute caustic soda to remove nitrophenol, then with water, and dried over calcium chloride in a vacuum desiccator. The mother-liquors and washings were evaporated down, acidified, and extracted with ether.

Yield :	61·1 g. of nitrophenetole, m. p. 56·5°	= 91·5%	of theor.
	3·3 g. of nitrophenol	= 6·0 ,,	,,
	20 c.c. of solution withdrawn for titration	= 1·0 ,,	,,
	Total	= 98·5 ,,	,,

This experiment confirmed the conclusion that *p*-chloronitrobenzene can be converted into nitrophenetole by heating at 60° for approximately 140 hours in 0·5 *N*-95% alcoholic potash, without the formation of any dichloroazoxybenzene, if the alcohol is free from acetaldehyde.

Under similar conditions, 65 g. of *o*-chloronitrobenzene, dissolved in 1 litre of aldehyde-free ethyl alcohol, gave a yield of 62·2 g. of *o*-nitrophenetole (90·3% of the theoretical), whilst 4 g. of *p*-chloronitrobenzene in 250 c.c. of methyl alcohol gave 3·750 g. of *p*-nitroanisole (96·5% of the theoretical).

No dichloroazoxybenzene was formed in either case.

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LXX.—*Action of Mercurous Nitrate on Chloroauric Acid.*

By WILLIAM BRANCH POLLARD.

THE action of mercurous nitrate on chloroauric acid has been stated to give (1) gold, or a mixture of gold and mercurous chloride (Proust, *Nicholson's J.*, 1806, **13**, 244), (2) a combination of aurous and mercuric oxides (Fischer, *Schweigger's J.*, 1829, **56**, 363), (3) aurous oxide (Figuier, *Ann. Chim. Phys.*, 1844, **11**, 336).

The author has studied the reaction under two distinct conditions; first, the reaction which occurs when an excess of some halide is present, and, secondly, the reaction which occurs in the absence of halides.

EXPERIMENTAL.

Action of Mercurous Nitrate on Chloroauric Acid in Presence of Halides.—Mercurous nitrate was prepared by shaking a solution of mercuric nitrate in dilute nitric acid with excess of mercury, a little carbamide being added to prevent the formation of nitrites. The solution was titrated as described below, and then diluted until 50 c.c. reduced exactly 0·5 g. of gold.

Gold (0·5 g.) was dissolved in 4 c.c. of aqua regia (3 : 1). The fumes were blown out with a current of air, but the excess of nitric and hydrochloric acids was not removed. The solution was diluted with 50 c.c. of water, 1 c.c. of concentrated hydrochloric acid was added, and mercurous nitrate solution run in. The black colour of the precipitate of metallic gold that instantly formed slowly changed to brown. The particles of the precipitate cohered on shaking, leaving the liquid clear. As the end-point was approached, the yellow colour of the chloroauric acid disappeared, the precipitate took on a transient purple tint, and finally white, mercurous chloride formed. During the titration, no evidence of reduction to the aurous state was obtained, even when a large amount of alkali-metal chloride was present (Diemer, *J. Amer. Chem. Soc.*, 1913, **35**, 552). Addition of such chlorides or of bromides or iodides appears to increase the velocity of the reaction. The amount of mercurous nitrate required to precipitate the gold when in combination with chlorine, bromine, or iodine was, however, practically identical in the three cases, provided there was sufficient halide to combine with the whole of the mercury present.

In order to obtain the quantitative relation between mercurous nitrate and chloroauric acid, the volume of solution required to precipitate 0·5 g. of pure gold was taken and precipitated with sodium chloride. The resulting mercurous chloride was equivalent to 2·0039 g. of mercurous nitrate as against 1·9947 g. required by the equation :

$$HAuCl_4 + 3HgNO_3 + 2HCl = 3HgCl_2 + 3HNO_3 + Au.$$

To test whether this relation held at very great dilutions, the mercurous nitrate and chloroauric acid were titrated at a dilution one hundred times as great as that employed above. The gold separated in the red, colloidal condition. It was flocculated with a little hydrochloric acid, and the end-point found by addition of *o*-tolidine (*Trans. Inst. Min. Met.*, 1923, **32**, 242), which gives a yellow colour with one part of chloroauric acid in twenty million parts of solution. At this dilution, the relationship found above still held.

From this experiment it is inferred that the precipitate which forms when strong solutions react consists of colloidal gold which has been flocculated by the acids and salts present in the liquid, and this would also account for the very marked adsorption effects which have been observed.

When 0·5 g. of the precipitated gold was shaken with a solution containing a few mg. of chloroauric acid, this substance was so completely adsorbed that it could not be detected in the solution.

The adsorbed substance reacted quite readily with solutions of reducing agents when these were applied to the precipitate.

When solutions of certain dyes were shaken with the precipitate, these became colourless, and in the case of methyl-red this was adsorbed more readily in an acid than in an alkaline solution.

In the course of these experiments it was noticed that if a very small amount of brucine or one of the quinine alkaloids was added to the chloroauric acid before precipitation with mercurous nitrate, the gold remained dispersed through the liquid and did not flocculate. Up to the present this result has not been observed except with the class of substances mentioned.

Action of Mercurous Nitrate on Chloroauric Acid in the Absence of Halides.—Gold (0·5 g.) was converted into chloroauric acid, and all excess of nitric and hydrochloric acids was removed; 50 c.c. of water were added and mercurous nitrate solution was run in. The precipitate did not "clear" on shaking and the end-point was difficult to find, but much less mercurous nitrate was needed to precipitate the gold completely in the absence of halides than in their presence.

To a fresh solution of chloroauric acid a little mercurous nitrate was added, in order to precipitate only a small part of the gold. The black precipitate, on standing over-night in the solution, was converted into metallic gold. The gold was separated from the solution, and a further amount of mercurous nitrate added. The black, colloidal precipitate which formed was centrifuged, and the clear solution, which had changed from yellow to reddish-brown, was further examined. When heated, a reddish-brown precipitate resembling ferric hydroxide formed, and the same substance was deposited when the solution was kept.

The substance was difficult to filter and wash, and after drying in a vacuum over sulphuric acid gained weight when exposed to the air. When heated, it gave off oxygen, water, and mercuric chloride, and left a residue of metallic gold. It dissolved in hydrochloric acid with the reformation of chloroauric acid.

If the equation for the reaction between mercurous nitrate and chloroauric acid is written omitting the hydrochloric acid from the left-hand side, this will require the addition of mercuric nitrate to the right-hand side:

$$HAuCl_4 + 3HgNO_3 = 2HgCl_2 + Hg(NO_3)_2 + HNO_3 + Au.$$

Now Proust (*loc. cit.*, p. 224) showed that when "gold chloride" was added to an excess of mercuric nitrate solution a yellow precipitate formed. This compound gave oxygen, water, mercuric chloride, mercurous chloride, and gold on heating. The brown

compound prepared by the author gave no mercurous chloride when heated.

On adding a small amount of mercuric nitrate to chloroauric acid, a slight darkening of the solution occurred. Further additions produced a reddish-brown solution similar to that previously obtained after centrifuging. When heated, a brown, colloidal precipitate separated identical with that previously described. The brown substance is therefore formed when chloroauric acid is in excess and Proust's yellow substance is formed when mercuric nitrate is in excess.

Proust explained the formation of his compound as being due to the very strong affinity of mercury for chlorine, which it is able to displace even from chloroauric acid.

Jacobson (*Compt. rend.*, 1908, **146**, 1213) has shown that silver nitrate also can remove chlorine from chloroauric acid with formation of a brown basic compound :

$$HAuCl_4 + 4AgNO_3 + 3H_2O = Au(OH)_3,4AgCl + 4HNO_3.$$

Attempts to discover the exact composition of the brown substance failed, as different preparations did not show sufficient agreement among themselves, and it is doubtful whether it has been prepared as yet in a state of purity. The following results, obtained by heating the substance in a Penfield tube, may, however, be taken as an approximate indication of its nature: Loss on heating (oxygen), 9·42; H_2O, 7·18; $HgCl_2$, 19·71; Gold (by difference), 63·69%.

The black precipitate formed by the action of mercurous nitrate on chloroauric acid which had been centrifuged out of the solution was now examined to see whether it consisted of a mixture of gold and the brown substance. After washing and drying, it was heated and gave off oxygen, water, and mercuric chloride and left a residue of gold. When it was treated with hydrochloric acid, chloroauric acid passed into solution and a residue of metallic gold was left. The black precipitate may therefore be regarded as a kind of " Purple of Cassius " in which stannic acid is replaced by the brown substance. It results from two reactions occurring simultaneously, which explains why, in the absence of halides, less mercurous nitrate is required to remove the gold completely from solution.

The author takes this opportunity of thanking Professor Carpenter and the staff of the Royal School of Mines for all the facilities which he has been afforded.

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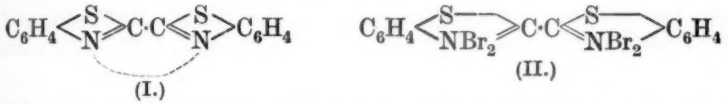
LXXI.—*Halogenation of* 2 : 6-*Dimethylbenzbisthiazole and of* 3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole.*

By Robert Fergus Hunter.

The slight unsaturation of the nitrogen atoms of the heterocyclic nuclei in 1 : 1-bisbenzthiazole (I) and the consequent great lability of the tetrabromide (II), which is so unstable that it decomposes appreciably into the original bisthiazole (I) and bromine on exposure to air for a few minutes (J., 1925, **127**, 1319), must, in view of the stability of 1-substituted benzthiazole bromides such as 1-phenylbenzthiazole tetrabromide (*loc. cit.*), clearly be due to the presence of the second thiazole nucleus.

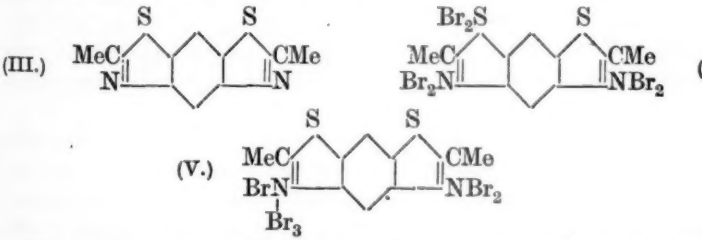


(I.) (II.)

That is to say that the two thiazole nuclei joined as in (I) by way of their μ-carbon atoms, mutually "saturate" each other.

Regarding this effect, it seems reasonable to suggest that the phenomenon is due to partial self-neutralisation of the valencies of the nitrogen atoms after the manner in which the central pairs of partial valencies in conjugated systems neutralise each other according to Thiele's theory (*Annalen*, 1899, **306**, 87). This supposition can be represented by means of a dotted line as in (I).

In view of this, it was clearly desirable to examine the unsaturation of the benzbisthiazole system in which the thiazole nuclei are separated from each other by a benzene ring which should inhibit or prevent the self-saturation effect displayed by 1 : 1-bisbenzthiazole. The example chosen was 2 : 6-dimethylbenzbisthiazole (III) (Edge, J., 1922, **121**, 772).



(III.) (IV.) (V.)

The reactive nitrogen atoms in this case are not linked by way of the ·N:C·C:N· system, but this is immaterial, since the supposed double bonds in the thiazole nucleus are aromatic in character, and the usual formula for the thiazole ring really can represent only *one*

of the transient phases of the intra-annular semi-aromatic heterocyclic nucleus.

2 : 6-Dimethylbenzbisthiazole in presence of excess of bromine readily passes into a bright yellowish-orange, relatively stable *hexabromide*, the most probable constitution of which is (IV). This bromo-additive compound is quite devoid of the properties of 1 : 1-bisbenzthiazole tetrabromide; for instance, it only loses appreciable halogen on exposure to the atmosphere for several days and is in many ways similar to the stable tribromo-additive compounds of the arylaminobenzthiazoles (J., 1925, **127**, 2024). The self-saturation effect of the thiazole nuclei is therefore removed by the intervention of the common aromatic nucleus. There is, however, another effect which arises in connexion with the unsaturation of the benzbisthiazole complex, namely, the alternation of the affinity effect of carbon chains (Flürscheim, *J. pr. Chem.*, 1902, **66**, 321; J., 1909, **95**, 718; 1910, **97**, 84; Ingold, J., 1925, **127**, 513), which operates in the manner described hereunder.

In the bromination of 2 : 6-dimethylbenzbisthiazole, the first reaction must necessarily consist in the addition of bromine to *one* of the ring nitrogen atoms. The consequent formation of the $:NBr_2$ group at once causes an alternation in affinity along the carbon chain connected to the second nitrogen atom, which therefore becomes partly saturated. Now there can be very little doubt, from the facts already described in connexion with the bromo-additive compounds of the benzthiazoles (*loc. cit.*), that the *centre* of unsaturation in a thiazole ring is the *nitrogen* atom. The obvious result is that in the bromination of the benzbisthiazole system one thiazole nucleus is much more *reactive* than the other, and hence one ring is responsible for the addition of four bromine atoms, whilst the other is fully satisfied by the addition of two. In this connexion, it does not matter whether the hexabromide has the constitution (IV) or the less probable formula (V).

The above is well borne out by the behaviour of 2 : 6-dimethylbenzbisthiazole towards other reagents such as methyl iodide; even in the presence of a large excess of methyl iodide, it will form only a monomethiodide (Edge, *loc. cit.*).

Since benzbisthiazole is in a sense a dithio-di-azo-heterocyclic compound, it was of interest to examine the thiodiazole complex. The example chosen was 3 : 5-diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole (Hector, *Ber.*, 1890, **23**, 357), which would be expected to pass under suitable conditions into the octabromide (VI).

(VI.) $\begin{matrix} Br_2PhN\text{–}C(NPh) \\ | \\ PhN{:}C\cdot NPhBr_2 \end{matrix}\!\!>\!SBr_4$ $\quad$ $\begin{matrix} I_2PhN\cdot C(NPh) \\ | \\ PhN{:}C\text{–}NPhI_2 \end{matrix}\!\!>\!SI_2$ (VII.)

Actually an *octabromide* having the expected properties was readily isolated as a bright red, crystalline compound, which gradually lost bromine on exposure to the atmosphere and was reduced by sulphurous acid (Hunter, *loc. cit.*) with regeneration of the original thiodiazole.

There are, however, alternative formulæ for this compound involving the $Br{\cdot}N{\cdot}Br{<}^{Br}_{Br}$ group. In view of the lesser affinity of iodine as compared with bromine for sulphur (compare Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826) and the facility iodine atoms have for combining with one another, which is greater even than that of bromine atoms, if the octabromide is indeed (VI), it might be expected that the thiodiazole on treatment with iodine would yield an additive compound of a *lower* order; whilst if the existence of the octabromide were due to the presence of the $Br{\cdot}N{\cdot}Br_3$ group, an octaiodide would be formed. Actually the only iodo-additive compound isolated was a *hexaiodide*, which is best represented by the formula (VII). Its formation is by no means a crucial test, but is in favour of the formulæ suggested for these additive compounds.

EXPERIMENTAL.

Dithioacetyl-*m*-phenylenediamine was prepared from diacetyl-*m*-phenylenediamine (20 g.) and oxidised with potassium ferricyanide according to Edge's directions (*loc. cit.*). The product isolated from the ethereal extract was allowed to crystallise spontaneously from light petroleum–alcohol and recrystallised (without distillation) from light petroleum, 2 : 6-dimethylbenzbisthiazole being thus obtained in shining prisms, m. p. 105°.

2 : 6-*Dimethylbenzbisthiazole Hexabromide.*—The benzbisthiazole (0·25 g.) dissolved in chloroform (5 c.c.) was slowly treated with bromine (0·3 c.c.). The solution was then either warmed and rapidly treated with a further quantity of bromine (0·3 c.c.), when the *hexabromide* crystallised, or the addition was continued in the usual way and the resulting solution warmed, cooled, and scratched. The *hexabromide* crystallised in small, yellowish-orange prisms, which were dried in a vacuum over phosphorus pentoxide; m. p. 117—118° (decomp.) (Found : Br, 68·2. $C_{10}H_8N_2Br_6S_2$ requires Br, 68·6%). The yield was nearly quantitative. The hexabromide showed no change on exposure to air for several hours; on exposure for 5 days, the compound lost appreciable bromine, very slowly becoming red. It was reduced in the usual way by sulphurous acid (*loc. cit.*). It dissolved readily in warm alcohol; on dilution and warming, acetaldehyde was evolved. A pure bromo-substitution derivative could not be isolated.

3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole*.—*s*-Diphenylthiocarbamide (15 g.) dissolved in absolute alcohol (300 c.c.) was gradually treated with bromine until a permanent yellow colour was obtained (Hugershoff, *Ber.*, 1903, **36**, 3121). The solution was filtered from coagulated sulphur into cold water (5 vols.), and the mixture made strongly alkaline with ammonia (*d* 0·880); the compound then separated in brittle, white granules. On crystallisation from ether, the thiodiazole separated in white plates, m. p. 136°, as recorded in the literature (yield, about 60%).

3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole Octabromide*.—The thiodiazole (1 g.) dissolved in chloroform (10 c.c.) was gradually treated with bromine (1 c.c.), and the resulting solution warmed and kept ½ hour. On scratching, the *octabromide* separated in glistening, orange-red prisms, which were dried in a vacuum over potassium hydroxide; m. p. 103—105° (Found: Br, 66·2. $C_{26}H_{20}N_4Br_8S$ requires Br, 66·6%). The bromide dissolved in glacial acetic acid, giving a solution which became colourless and evolved bromine and hydrogen bromide on prolonged boiling. The solution, on being made alkaline, furnished a product which crystallised from alcohol, on persistent scratching, in minute prisms, m. p. 200° (decomp.; after sintering at 110°). The quantity was much too small for investigation, but the product was doubtless an impure bromo-substitution derivative (*loc. cit.*).

3 : 5-*Diphenylimino*-2 : 4-*diphenyltetrahydro*-1 : 2 : 4-*thiodiazole Hexaiodide*.—The thiodiazole (3·8 g.) dissolved in 20 c.c. of glacial acetic acid was gradually added to a warm solution of iodine (5 g.) in the same solvent (250 c.c.), and the resulting solution warmed and kept for 3 hours; a part of the *iodo*-additive compound then separated in small, black, glistening prisms, which were washed with a little acetic acid and dried in a vacuum; m. p. 120°. A second crop separated over-night in shining, black prisms having a dark green reflex, which were thoroughly washed with glacial acetic acid and dried in a vacuum as before; m. p. 122° (decomp.) (Found: I, 66·5. $C_{26}H_{20}N_4I_6S$ requires I, 66·8%).

The hexaiodide was practically unacted upon by sulphurous acid owing to its insolubility, but was readily reduced by sulphur dioxide in acetic acid solution. It was readily decolorised by sodium thiosulphate [0·1120 g. in glacial acetic acid (redistilled over potassium permanganate) required 27·5 c.c. of 1·97*N*/100-sodium thiosulphate. I, 57·4%]. The iodide was readily soluble in ether, ethyl acetate, and alcohol, but could not be recrystallised.

A number of experiments were also carried out on the halogenation of 3 : 5-di-*p*-tolylimino-2 : 4-di-*p*-tolyltetrahydro-1 : 2 : 4-thiodiazole, m. p. 138°, which was obtained in the same way as the

phenyl derivative (Hugershoff, *loc. cit.*), but definite compounds could not be isolated; bromination and iodination in different solvents and under various conditions led to uncrystallisable gums or resins.

The author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for the kind interest he has taken in this work.

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LONDON, S.W. 7. [*Received, November 11th,* 1925.]

LXXII.—*Bromination of some 5-Substituted 1-Phenylbenzthiazoles.*

By ROBERT FERGUS HUNTER.

THE bromination of 1-phenylbenzthiazole has been investigated by Bogert and Abrahamson (*J. Amer. Chem. Soc.*, 1922, **44**, 826), who obtained a red unstable tetrabromo-additive compound, to which they assigned the constitution (I), which on boiling with dilute acetic acid yielded 5-bromo-1-phenylbenzthiazole.

The tetrabromide thus prepared gradually loses bromine on exposure to air, becoming almost colourless, and is instantaneously reduced to 1-phenylbenzthiazole by sulphurous acid and sodium bisulphite (compare **J.**, 1925, **127**, 1319, 1488, 2023). The compound must therefore be a *perbromide;* and may have the constitution (I) or (II), the latter being analogous to that of the tetrabromides of pyridine and quinoline (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558; Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124).

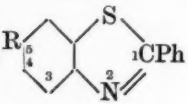
(I.) $C_6H_4\langle\begin{matrix}SBr_2\\NBr_2\end{matrix}\rangle CPh$ $\qquad$ $C_6H_4\langle\begin{matrix}S\text{———}\\NBr(Br_3)\end{matrix}\rangle CPh$ (II.)

The formation of a *di-iodo*-additive compound and not a *tetraiodo*-derivative by 1-phenylbenzthiazole (*loc. cit.*) is in favour of the formula (I); the slight ionisation of 1-phenylbenzthiazole tetrabromide in glacial acetic acid solutions is, moreover, in accordance with the presence of a "thiazonium" sulphur atom as in (I), but the question cannot be fully discussed until the behaviour of substances such as dimethyl sulphide dibromide (Cahours, *Annalen*, 1865, **135**, 355) has been thoroughly reinvestigated.

The passage of phenylbenzthiazole tetrabromide into 5-bromo-1-phenylbenzthiazole (Bogert and Abrahamson, *loc. cit.*) suggests that there is probably an intimate connexion between the ring nitrogen atom (2) of the fused thiazole nucleus and the carbon atom (5) of the homocyclic ring of the benzthiazole system. The transformation is indeed a sort of "para-migration," and no doubt takes

place by way of a para-bridged intra-annular phase of the benzene ring. It might be expected, therefore, that the substitution of groups of varying polar character on the carbon atom (5) would have a profound effect on the unsaturation of the nitrogen atom (2) as exhibited by a tendency towards the formation of bromo-additive compounds (compare also Fries, *Annalen*, 1906, **346**, 128). It is, moreover, clear that this effect will manifest itself whether the tetrabromide has the constitution (I) or (II), for in the former case the effect on the nitrogen atom (2) will be communicated to the sulphur atom (7) by way of the well-known alternation of affinity effect in carbon chains.

Actually, it was found in connexion with the 5-substituted 1-phenylbenzthiazoles (III) that the electro-polar character of the 5-substituent has a remarkable effect on the tendency of these bases to form bromo-additive compounds.

(III.) 

$NO_2 \cdot C_6H_3 \langle \overset{S}{\underset{NBr_2}{}} \rangle CPh$ (IV.)

Thus the negative nitro-group (R = NO_2) in 5-nitro-1-phenylbenzthiazole depresses the unsaturation of the thiazole system to such an extent as to render the formation of bromo-additive compounds impossible in acetic acid solutions, and to allow the formation only with considerable difficulty of the dibromide (IV) in chloroform. The less negative bromine atom in 5-bromo-1-phenylbenzthiazole (R = Br), on the other hand, allows the formation of a very unstable tetrabromo-additive compound with difficulty; whilst the positive amino-group (R = NH_2) enhances unsaturation of the thiazole system in 5-amino-1-phenylbenzthiazole to such an extent as to cause the immediate formation of a stable tetrabromide in the case of the latter benzthiazole derivative.

Bromination of 1-phenylbenzthiazole in chloroform gave rise to two isomeric forms of the tetrabromo-additive compound (m. p. 126° and 153°), just as di-β-naphthylthiocarbamide yields two forms of the hexabromide of 2-β-naphthylamino-α-naphthathiazole (Hunter, J., 1925, **127**, 2273). Both forms of the tetrabromide were reduced by sulphurous acid and passed into the substitution derivative on boiling with dilute alcohol and acetic acid (*loc. cit.*). It is highly probable that the lower-melting tetrabromide is identical with that formed in the bromination of the phenylbenzthiazole in glacial acetic acid solution, which usually commences to sinter at about 130°.

The bromo-additive compounds of the benzthiazole series, like the *p*-bromophenyltrimethylammonium perhalides (Reade, J.,

1924, **125**, 150), decompose rapidly at the temperature of fusion (and frequently below this : J., 1925, **127**, 2026), and therefore the melting point is not a real criterion of purity. For this reason, too much stress cannot be laid on the isolation of isomeric forms of the compounds, for the melting point (which is also the decomposition point) is appreciably affected by the crystalline form of the compound.* It is hoped to investigate this question more fully at an early date.

EXPERIMENTAL.

1-Phenylbenzthiazole was prepared from benzylideneaniline by Bogert and Abrahamson's method (*loc. cit.*). The finely crushed melt was added in a slow stream to boiling 60% sulphuric acid, and the resulting mixture boiled for an hour (water being added to make up for that lost by evaporation). The acid extract was filtered into cold water (10 vols.), and the precipitated base was washed, dried at 70°, dissolved in the minimum of boiling alcohol (to remove resinous material), and the filtered solution poured into cold water. The product, after drying, crystallised from light petroleum–alcohol (3 : 1) in pale yellow prisms, m. p. 114°, having the odour of geraniums and other properties described by Hofmann (*Ber.*, 1879, **12**, 2359).

Bromination. (A). Phenylbenzthiazole (2 g.) dissolved in glacial acetic acid was gradually treated with bromine (Bogert and Abrahamson, *loc. cit.*). The tetrabromide separated in red needles or prisms, which were dried in a vacuum over potassium hydroxide; m. p. 137° after sintering at 130° (Found : Br, 60·6. Calc., Br, 60·3%). On boiling with dilute acetic acid or alcohol, 5-bromo-1-phenylbenzthiazole was produced which crystallised from glacial acetic acid in shining prisms, m. p. 152°.

Since this method of preparing the tetrabromide invariably gave resinous products, the bromination of 1-phenylbenzthiazole in chloroform was examined.

(B). Phenylbenzthiazole (2 g.) dissolved in chloroform (30 c.c.) was gradually treated with bromine (2 c.c.), and the resulting solution boiled, and cooled in ice. On scratching, reddish-brown needles of phenylbenzthiazole tetrabromide separated which were dried in a vacuum over potassium hydroxide; m. p. 126° (decomp.) (Found : Br, 60·6. $C_{13}H_9NBr_4S$ requires Br, 60·3%). The filtrate from this compound, on concentration and cooling, furnished slender, orange needles of a second *tetrabromide*, which were dried as before; m. p. 153° (decomp.) (Found : Br, 59·8%).

* Thus specimens of 1-anilinobenzthiazole tetrabromide crystallised from chloroform under different conditions may have melting points anywhere between 112° and 117° (Hunter, J., 1925, **127**, 2025).

5-Nitro-1-phenylbenzthiazole was obtained by the direct nitration of phenylbenzthiazole with nitric acid (*d* 1·5) and by nitration with a mixture of sulphuric acid and nitric acid (*d* 1·4) as described in the literature (*loc. cit.*). After two crystallisations from glacial acetic acid, the nitrobenzthiazole was obtained in small, orange prisms, m. p. 188°. In both cases the yield exceeded 90%.

5-Nitro-1-phenylbenzthiazole Dibromide.—5-Nitro-1-phenylbenzthiazole was recovered unchanged after a saturated solution of the compound in glacial acetic acid had been treated with bromine. The nitrophenylbenzthiazole (2 g.) suspended in chloroform (40 c.c.) was gradually treated with bromine (2 c.c.); after ½ hour, the mixture was boiled and filtered, and the filtrate kept over-night. The somewhat pasty precipitate of the *dibromide* was collected and agitated with an ethereal solution of bromine, when vermilion prisms were obtained which were dried in the usual way. They softened at 120° and melted at 144° (Found: Br, 37·8. $C_{13}H_8O_2N_2Br_2S$ requires Br, 38·5%). The dibromide lost bromine on exposure to air and was reduced by sulphurous acid in the usual way. On boiling with dilute acetic acid, bromine was evolved with regeneration of the original nitrobenzthiazole.

5-Bromo-1-phenylbenzthiazole Tetrabromide.—When 5-bromo-1-phenylbenzthiazole (1 g.) in chloroform (12 c.c.) was gradually treated with bromine (1·6 c.c.), a dark red solution was obtained which deposited red prisms of a tetrabromo-additive compound, m. p. 206—208° (decomp.) (Found: Br, 64·8. $C_{13}H_8NBr_5S$ requires Br, 65·6%). This compound was most unstable and lost bromine immediately on exposure to air; bromine was also eliminated with regeneration of the original 5-bromo-substitution derivative by boiling with dilute acetic acid, or by treating with sulphurous acid. By using a smaller quantity of bromine, red needles of another bromide were obtained which changed colour at 85°, became orange at 110°, and showed signs of loss of bromine at 175°; m. p. 208° (decomp.). The bromine content was that of a tribromo-additive compound [Found: Br, 60·9. $(C_{13}H_8NBr_4S)_2$ requires Br, 60·4%]. This bromide had similar properties to the tetrabromide already described; it was converted into 5-bromo-1-phenylbenzthiazole by sulphurous acid or by boiling dilute acetic acid.

5-Amino-1-phenylbenzthiazole, prepared by reduction of the 5-nitro-derivative (*loc. cit.*), on repeated crystallisation from boiling aniline or toluene, was obtained in small prisms, m. p. 208°, as recorded. In cases where the reduction had proceeded too vigorously, the product after crystallisation was very dark and resinous; attempts were therefore made to work up the base by way of the benzylidene derivative (*loc. cit.*). The product separated from

alcohol in pale yellow plates, m. p. 190° (39° above the recorded temperature); the m. p. was unaltered by recrystallisation. 5-Benzylideneamino-1-phenylbenzthiazole prepared from pure 5-amino-1-phenylbenzthiazole had the melting point of 151° recorded in the literature. The nature of the high-melting product has not yet been investigated.

5-Amino-1-phenylbenzthiazole Tetrabromide.—5-Amino-1-phenylbenzthiazole (1 g.) suspended in chloroform (30 c.c.) was gradually treated with bromine (1·1 c.c.) dissolved in a small amount of the same solvent; an ochre-coloured precipitate of the bromo-additive compound appeared on the addition of the first drop of halogen. The mixture was boiled and filtered, the residue digested with dry ether containing bromine, and the product dried in the usual way. A dark brown, microcrystalline powder was thus obtained which melted at 216° after showing colour change between 180° and 190° (Found: Br, 60·1. $C_{13}H_{10}N_2Br_4S$ requires Br, 58·6%). The filtrate from this bromide, on slight concentration, furnished red prisms of another *tetrabromide*, m. p. 210—211°, which were dried in a vacuum as before (Found: Br, 60·3%). The brown tetrabromide was remarkably stable to air and in this respect resembled the dibromide of 4′-amino-1-phenyl-5-methylbenzthiazole (J., 1925, **127**, 1318). On boiling with acetic acid a red solution was obtained which deposited prisms of the second tetrabromide, m. p. 210°. Both bromides were reduced in the usual way by sulphurous acid, etc. On boiling the red crystals with dilute acetic acid, a dark product was obtained; this was digested with dilute alkali, dried, and repeatedly extracted with boiling alcohol, which removed a purple impurity. The brown residue was washed with ether and dried. It appeared to be an impure bromo-substitution product and softened at about 170°; its analysis corresponded most closely with a *dibromo*-derivative (Found: Br, 39·3. $C_{13}H_9N_2Br_2S$ requires Br, 41·8%). The purple alcoholic extracts on evaporation furnished a quantity of dark-coloured product insufficient for investigation.

The experiments here described were commenced early in 1924 with the object of studying the effect of the substitution of groups of varying polar and spatial character on the unsaturation of the fused thiazole nucleus. Since the work has been temporarily abandoned, it has seemed desirable to publish the results so far obtained.

The author desires to express his gratitude to Professor J. F. Thorpe and Dr. M. A. Whiteley for the kind interest they have taken in this work.

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LXXIII.—*Studies in Colour and Constitution. Part I. The Influence of the Methylthiol Group, alone and in Conjunction with the Methoxy-group.*

By Herbert Henry Hodgson and Frederick William Handley.

The superior bathochromic influence of the methylthiol group in comparison with the methoxy-group was discovered by Brand (*Ber.*, 1909, **42**, 3463). The work of Waldron and Reid (*J. Amer. Chem. Soc.*, 1923, **45**, 2399) and of Foster and Reid (*ibid.*, 1924, **46**, 1936), however, indicated this influence was stronger or weaker than that of the methoxy-group according as the methylthiol group was in the para- or ortho-position with respect to it.

Dyes were prepared from 2- and 4-thioanisidines by one of the authors (H. H. H.) in 1918 (Brit. Pat. 235334 of 1924), and his study of meta-halogenated phenols has afforded the opportunity of comparing the bathochromic effects of the methylthiol and methoxy-groups in ortho- and para-positions, and vice versa, in the same amine.

For this purpose, the action of sodium disulphide on 3-chloro-2-, -4-, and -6-nitrophenols (Hodgson and Moore, J., 1925, **127**, 1925) has been investigated. No replacement of chlorine in the free phenols and in 3-chloro-2-nitroanisole took place, but the methyl ethers of 3-chloro-4- and -6-nitrophenols were readily converted into disulphides. These ethers were prepared in good yield by Haworth and Lapworth's method (J., 1923, **123**, 2986) and have been described by Hodgson and Moore (this vol., p. 157). Conversion of the disulphides into thioethers and subsequent reduction produce respectively 4-anisidine-2- and 2-anisidine-4-methyl thioethers, in which the positions of the methoxy- and methylthiol groups are interchanged.

Azo-dyes were prepared from the above amines with Schäffer salt, R-salt, and H-acid (in alkaline solution) as second components, and also, for comparison purposes, from 2- and 4-anisidines and 2- and 4-thioanisidines. From the dyeings on wool, the colorimetric estimation of the dye solutions by the Lovibond tintometer, and the colours given by the solid dyes with concentrated sulphuric acid, the superiority of the bathochromic influence of the methylthiol group in the para-position was found to be most pronounced. The methoxy-group in the Schäffer and R-salt dyes, however, exhibited the converse influence, *i.e.*, it produced the optimum effect when it was in the ortho-position. The *o*-methylthiol and *p*-methoxy-groups appear to produce the same effect. The maximum effect was obtained with the *p*-methylthiol group in conjunction with an

o-methoxy-group, *viz.*, very pronounced violet colour with the Schäffer and R-salt dyes and an almost indigo-blue colour with the H-acid dye. Chlorine exerts the same influence as the methylthiol group, but to a less degree; the shades, however, are brighter. In all cases the dyes from 4-thioanisidine are the strongest in tinctorial power.

Experimental.

3-*Chloro*-4- *and* -6-*nitroanisoles*.—The respective chloronitrophenols (8 g.) dissolved in xylene (40 c.c.) were heated under reflux on the water-bath for 8 hours in presence of potassium carbonate (10 g.), and methyl sulphate (10 c.c.) was gradually added. The mixture was rendered strongly alkaline and steam-distilled; xylene and a little ether passed over first and were followed by the main bulk (yield 7 g.; 81%).

4-*Chloro*-2- *and* 2-*Chloro*-4-*anisidines*.—The above ethers (1 g.) were each heated under reflux on the water-bath with concentrated hydrochloric acid (5 c.c.) and water (15 c.c.), with gradual addition of granulated tin (3 g.). After the ether had dissolved, the mixture was made alkaline and the products were removed by steam distillation. For convenience, the hydrochlorides were prepared (yield 0·8 g.). They formed long needles, m. p. 238° and 228°, respectively (Found: Cl, 36·4 and 36·5. C_7H_8ONCl,HCl requires Cl, 36·6%).

2 : 2′-*Dinitro*- *and* 4 : 4′-*Dinitro*- 5 : 5′-*dimethoxydiphenyl Disulphides*.—3-Chloro-4- and -6-nitroanisoles (8 g.) were each dissolved in alcohol (50 c.c.) and gently boiled under reflux during the cautious addition of aqueous sodium disulphide (crystallised sodium sulphide, 6 g.; sulphur, 0·8 g.; water, 40 c.c.); heating was then continued for 4—5 hours. The respective disulphides separated and the contents were filtered hot, unchanged nitroanisole being removed by warm alcohol (yield 6·5—7 g.; 88—90%).

2 : 2′-*Dinitro*-5 : 5′-*dimethoxydiphenyl disulphide* is insoluble in water, alcohol, or benzene, but soluble in carbon disulphide or glacial acetic acid, from which it crystallises in white needles, m. p. 152° (uncorr.); these rapidly turn yellow in sunlight (Found: N, 7·4; S, 18·0. $C_{14}H_{12}O_6N_2S_2$ requires N, 7·6; S, 17·4%). The last trace of free sulphur was retained even after repeated crystallisation. Concentrated aqueous or alcoholic alkali hydroxides give violet-red solutions. Concentrated sulphuric acid gives a pale yellow solution in the cold, unchanged by moderate heating or dilution. Chlorosulphonic acid gives a crimson solution in the cold, which becomes yellow on heating and remains so on dilution, whilst oleum (23% SO_3) produces a brownish-yellow colour, which

changes to yellow on heating and lemon-yellow on subsequent dilution.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenyl disulphide* resembles the preceding isomeride in solubility. It crystallises from glacial acetic acid in white, glistening micro-plates, m. p. 194° (uncorr.) (Found : N, 7·6; S, 17·9%). The solutions in alkalis are deep red. Concentrated sulphuric acid produces an orange-yellow colour in the cold, which becomes successively red, brown, and green on heating, and brownish-purple on subsequent dilution. Chlorosulphonic acid or oleum (23%) produces a green colour in the cold, which changes to reddish-brown on heating; a reddish-brown precipitate forms on dilution.

2-*Nitro- and* 4-*Nitro*-5-*methoxythioanisoles*.—The above disulphides (2 g.) were each heated on the water-bath for 15 minutes with alcohol (10 c.c.), crystallised sodium sulphide (1 g.), sodium hydroxide (2·4 g.), and water (10 c.c.). The mixture was then stirred into water (35 c.c.), filtered if necessary, and warmed with methyl sulphate (2—2·5 c.c.), when the thioanisole separated (yield 2 g.; 92%).

2-*Nitro*-5-*methoxythioanisole* is insoluble in cold but slightly soluble in hot water and is very slowly volatile in steam. It crystallises from alcohol in yellow needles, m. p. 112—113° (uncorr.), and is very slowly decomposed by nitric acid (Found : N, 7·2. $C_8H_9O_3NS$ requires N, 7·0%). The crimson solution in concentrated sulphuric acid becomes violet on heating and thereafter yellow on dilution. The corresponding colorations produced by oleum (23%) and chlorosulphonic acid are blood-red, reddish-brown and yellow, and blue, violet and yellow, respectively.

4-*Nitro*-5-*methoxythioanisole* resembles the preceding isomeride in solubility and volatility in steam, but crystallises from alcohol in paler yellow needles, m. p. 79—80° (uncorr.) (Found : N, 6·9%). The colorations produced by solution, heating, and subsequent dilution are : for concentrated sulphuric acid, scarlet, blood-red to reddish-violet, blood-red; for oleum, chocolate-brown, blood-red, yellow; for chlorosulphonic acid, red, orange, yellow.

2-*Anisidine*-4-*methyl- and* 4-*Anisidine*-2-*methyl Thioethers*.—The respective nitro-compounds (2 g.) were heated under reflux with granulated tin (4 g.), concentrated hydrochloric acid (10 c.c.), and water (10 c.c.) until all had dissolved. The solution was made distinctly alkaline with sodium hydroxide and steam-distilled. In both cases, the bases passed over as oils, but only 2-anisidine-4-methyl thioether crystallised on standing. The 4-anisidine isomeride was converted into the hydrochloride.

2-*Anisidine*-4-*methyl thioether* is very soluble in alcohol and

crystallises from water in white, feathery needles, m. p. 44° (uncorr.), which become discoloured in air (yield 1·3 g.; 77%) (Found: N, 8·5; S, 19·1. $C_8H_{11}ONS$ requires N, 8·3; S, 18·9%). Concentrated sulphuric acid gives a yellow solution which remains unchanged on heating or dilution. The pale violet solution in oleum changes to deep violet on warming, but becomes colourless on prolonged heating.

The *hydrochloride* crystallises from hydrochloric acid in colourless needles which turn pink in air; m. p. 235° (approx.) (Found: Cl, 17·5; S, 15·2. $C_8H_{11}ONS,HCl$ requires Cl, 17·3; S, 15·6%).

4-*Anisidine*-2-*methyl thioether* is an oil which is very soluble in alcohol, but only slightly so in water. Concentrated sulphuric acid gives a violet solution in the cold, which becomes reddish-violet on heating. The corresponding colorations with oleum and chlorosulphonic acid are blue-violet and reddish-purple and purple and reddish-purple, respectively.

The *hydrochloride* forms white needles, m. p. 210—211°, which become steel-grey on exposure to light (Found: N, 7·4; Cl, 17·25; S, 15·3. $C_8H_{11}ONS,HCl$ requires N, 7·0; Cl, 17·3; S, 15·6%).

The Dyes.—These were prepared in the usual way and sodium chloride was removed as completely as possible.

Dyeing trials. Wet strips of wool (2·5 g.) were introduced into a bath of water (250 c.c.) containing the dyes (0·025 g.), sodium sulphate (0·25 g.), and sulphuric acid (0·05 g.). The solution was gradually heated to the boiling point and there maintained until the dyeing was complete.

Dye solutions. These were evaluated in terms of red, yellow, and blue components by means of the Lovibond tintometer.

The colours produced by sulphuric acid on the dry dye powders were also examined.

For convenience, the dyes are referred to by the attached numerals, which indicate the particular amine employed: 2-anisidine (I), 4-anisidine (II), 4-chloro-2-anisidine (III), 2-chloro-4-anisidine (IV), 2-anisidine-4-methyl thioether (V), 4-anisidine-2-methyl thioether (VI), 2-thioanisidine (VII), 4-thioanisidine (VIII).

The order of increasing redness is from left to right.

Results.

Dye.	Experiment.	Order.
From Schäffer Salt.	Wool dyeing.	V, VIII, I, III, VII, IV, II, VI. (Red-violet) (Red) (Scarlet to orange)
„ „ „	Lovibond.	V, VIII, VI, III, I, IV, VII, II.
„ „ „	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. (Blue) (Violet) (Crimson)
„ R-Salt.	Wool dyeing.	V, VIII, III, I, VI, II, VII, IV. (Violet) (Bluish-red) (Red with gradual increase of yellow)

Dye.	Experiment.	Order.
From R-Salt.	Lovibond.	V, VIII, III, I, VI, IV, II, VII.
„ „	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. (Blue) (Violet) (Crimson)
„ H-Acid.	Wool dyeing.	V, VIII, VI, II, VII, III, IV, I. (Indigo-blue) (Red-violet) (Violet-red)
„ „	Lovibond.	V, VI, VII, VIII, IV, I, II, III.
„ „	Sulphuric acid.	VIII, V, IV, VI, II, III, I, VII. (Blue) (Violet)

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LXXIV.—*Iodination in the Carbazole Series.*

By STANLEY HORWOOD TUCKER.

OXIDATION of carbazole brought about the formation of the two dicarbazyls described by Perkin and Tucker (J., 1921, **119**, 216). Attempts to synthesise these compounds and their possible isomerides have led to the preparation of iodo-derivatives of carbazole and of its alkyl and acyl compounds. Except the iodo-compounds described by Stevens and Tucker (J., 1923, **123**, 2146) and Tucker (J., 1924, **125**, 1144), the only one prepared was di-iodocarbazole (Classen, D.R.-P. 81929, 1894). Classen's description of it is inaccurate.

3-Iodocarbazole has been synthesised from 3-aminocarbazole (Tucker, *loc. cit.*). It has now been obtained directly from carbazole by the action of potassium iodide and iodate in glacial acetic acid solution, working according to the equation $3C_{12}H_9N + 2KI + KIO_3 + 3CH_3{\cdot}CO_2H = 3C_{12}H_8NI + 3H_2O + 3CH_3{\cdot}CO_2K$, except that potassium iodate and acetic acid are used in excess. The iodine at first liberated is gradually used up and the solution finally becomes colourless. The 3-iodocarbazole so obtained is mixed with considerable quantities of di-iodocarbazole. Much of the 3-iodocarbazole can be separated by crystallisation, but to obtain the di-iodocarbazole it is necessary to utilise the acetyl or benzoyl derivative.

The di-iodocarbazole described by Classen, and prepared by a different method from the above, was alleged to be yellow, and to melt at 184°; repetition of his work gave only colourless di-iodocarbazole, m. p. 202—204°. The di-iodocarbazole is almost cer-

tainly 3 : 6-di-iodocarbazole by analogy with other disubstitution products of carbazole.

Iodination of 9-methyl and 9-ethylcarbazole by the above method likewise gives the respective 3-iodo- and di-iodo-compounds.

Like carbazole and the 9-alkylcarbazoles, 9-benzoylcarbazole may be iodinated by means of potassium iodide and iodate in glacial acetic acid to give a corresponding yield of its 3-iodo-derivative, but the discharge of the iodine coloration is much less rapid, *viz.*, 10 minutes for carbazole (less for the 9-alkylcarbazoles) and 75 minutes for 9-benzoylcarbazole. Incomplete iodination of 9-toluene-*p*-sulphonylcarbazole took place under similar conditions in 2 hours. Iodination of 9-acetylcarbazole did not proceed to any appreciable extent. Judged, therefore, by this process of iodination, resistance to replacement of hydrogen in the carbazole nucleus increases in the order 9-alkylcarbazoles, carbazole, 9-benzoyl-, 9-toluene-*p*-sulphonyl-, and 9-acetyl-carbazole. All may be iodinated by the action of the more vigorous iodinating reagent, iodine and nitric acid in glacial acetic acid (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292). The 9-alkylcarbazoles and carbazole give at once iodonitro-compounds.

There is no evidence of the formation of any 1-iodo-derivatives.

Experimental.

Iodination of Carbazole.—(i) *Using potassium iodide and potassium iodate in glacial acetic acid.* Pure * carbazole (16·7 g.) was dissolved in boiling glacial acetic acid (250 c.c.), and potassium iodide (11 g.) added. The solution was cooled somewhat, finely-powdered potassium iodate (16 g., *i.e.*, approximately twice the amount theoretically required) added, and the mixture then boiled until it acquired a clear straw-coloured tint (10 minutes). The hot solution was decanted from the undissolved potassium iodate and allowed to cool slowly to 45°. The faintly brown, nacreous plates which separated were rapidly filtered off and recrystallised from glacial acetic acid (or alcohol), the solution being allowed to cool to 45° and filtered as before from the white, nacreous plates (10—12 g.) of 3-iodocarbazole, m. p. 192—194°. From the united filtrates, on standing, there separated 3 : 6(?)-*di-iodocarbazole*, m. p. 202—204° (Found : I, 60·6. $C_{12}H_7NI_2$ requires I, 60·6%), but since the

* The yield of 3-iodocarbazole is considerably diminished if the carbazole used is impure. Pure carbazole exhibits a faint violet fluorescence, and melts at 238° when the melting point is taken in the usual way with a long emergent stem; when taken with a short Anschütz thermometer having the stem immersed, the m. p. is 245° (compare Graebe and Glaser, *Ber.*, 1872, **5**, 12; Täuber, *ibid.*, 1891, **24**, 2597; Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274T; Senseman and Nelson, *Ind. Eng. Chem.*, 1923, **15**, 382).

quantity was very small it was found better to proceed thus: The united filtrates were poured into water and the white precipitate was dried (16·5 g.). Crystallisation of this product from various solvents did not raise the melting point above 160°. Accordingly, the material was boiled with acetic anhydride and a trace of concentrated sulphuric acid. After a short time, a white, crystalline precipitate suddenly separated. It was washed with boiling glacial acetic acid and recrystallised several times from benzene. 3 : 6(?)-*Di-iodo*-9-*acetylcarbazole* was thus obtained in long, colourless needles, grouped in porcupine-like tufts, m. p. 224—225° (Found: I, 55·4. $C_{14}H_9ONI_2$ requires I, 55·1%). The acetic anhydride filtrate was poured into water, and the precipitate produced was crystallised from glacial acetic acid. Colourless needles separated in rosettes very like those of 3-iodo-9-acetylcarbazole (m. p. 145—147°), but repeated crystallisation from glacial acetic acid, alcohol, and benzene–light petroleum failed to raise the melting point above 133—137°. However, by boiling this material with alcoholic potassium hydroxide solution for a few minutes, pouring into water, and recrystallising the precipitate from glacial acetic acid as described under the isolation of 3-iodocarbazole, a good yield of pure 3-iodocarbazole was obtained.

The separation of 3-iodocarbazole and 3 : 6-di-iodocarbazole can also be effected by benzoylation.* The product (16·5 g., obtained after removal of 3-iodocarbazole by preliminary crystallisation) was dissolved in acetone (100 c.c.), and powdered potassium hydroxide (12 g.) added. The mixture was boiled, allowed to cool slightly, and benzoyl chloride (10 c.c.) added slowly; a vigorous reaction took place. The liquid was swirled round after each addition of benzoyl chloride, but not shaken vigorously until the end; it was then poured into water. The pale brown oil at first precipitated, which solidified to a pasty, white solid, was dissolved in acetone. The crystals which separated were much less soluble in acetone than the crude material, and were best recrystallised

* The method of benzoylation of carbazole (Stevens and Tucker, *loc. cit.*, p. 2146) proceeds as given for the quantities used, but with larger quantities of carbazole (16·7 g., *e.g.*) vigorous shaking must be avoided; the liquid, after addition of benzoyl chloride, should be gently swirled, and only shaken finally. (The author is indebted to Mr. A. Kent, M.A., B.Sc., of this Department, for this observation.) To separate 9-benzoylcarbazole from unchanged carbazole, the mixture is dissolved in benzene and allowed to cool; carbazole then separates, and more is obtained by concentrating the filtrate to half-bulk. The benzene (in which 9-benzoylcarbazole is very soluble) is evaporated and the residue crystallised from much alcohol. Pure 9-benzoylcarbazole, m. p. 98°, is obtained. If carbazole is not thus removed, the m. p. of the product does not rise above 90° even after repeated crystallisation. The above applies generally to all benzoylations described in this paper.

from pyridine to which a drop of water was added, or from carbon tetrachloride, giving 3 : 6-*di-iodo*-9-*benzoylcarbazole*, m. p. 204—205° (Found : I, 48·9. $C_{19}H_{11}ONI_2$ requires I, 48·6%). Concentration of the acetone filtrate gave a further crop, the total yield of pure material being 3·2 g. The very concentrated acetone filtrate deposited 3-*iodo*-9-*benzoylcarbazole* (0·8 g.), m. p. 145—146° (Found : I, 31·9. $C_{19}H_{12}ONI$ requires I, 32·0%). A thick, brown oil was left. When macerated with cold glacial acetic acid, much dissolved; but a yellow powder remained insoluble. After several crystallisations from carbon tetrachloride or light petroleum, it melted at 184—186°, but appears to be 3-iodocarbazole (0·2 g.).

(ii) *Using iodine and yellow mercuric oxide in alcohol* (Classen, *loc. cit.*). Classen's procedure was followed as described, then the product was recrystallised three times from carbon tetrachloride, and red crystals were obtained, m. p. 201—204°. These were boiled in glacial acetic acid with animal charcoal, and recrystallised from alcohol in colourless, long, rectangular laminæ of 3 : 6-di-iodocarbazole, m. p. 202—204°.

3-*Iodo*-9-*acetylcarbazole*.—The best method of preparing this compound is acetylation of 3-iodocarbazole (Tucker, *loc. cit.*); but it is readily prepared from 9-acetylcarbazole thus : 9-Acetylcarbazole (2 g.) and iodine (1 g.) were dissolved in glacial acetic acid (40—50 c.c.), the solution cooled to about 60°, and a solution of 2 c.c. of concentrated nitric acid in 8 c.c. of glacial acetic acid added drop by drop. When 1 c.c. of the solution had been added, the mixture was boiled and the addition of the nitric acid solution continued at intervals during the boiling until the iodine coloration had just vanished. Yellow crystals separated on cooling. They recrystallised from glacial acetic acid, and from alcohol, in colourless crystals, slightly soluble in light petroleum. Attempts to iodinate 9-acetylcarbazole by means of iodide and iodate, as for the iodination of carbazole, showed that after several hours' boiling some iodine had been used up, but no iodo-compounds could be isolated.

3 : 6(?)-*Di-iodo*-9-*acetylcarbazole* was prepared from 3 : 6(?)-di-iodocarbazole by boiling with acetic anhydride containing a trace of concentrated sulphuric acid. The solution set at once to a pure white solid, which crystallised from benzene, much glacial acetic acid, or alcohol in clusters of long needles, m. p. 224—225°. It was readily hydrolysed by boiling alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

3-*Iodo*-9-*benzoylcarbazole* was prepared (*a*) from 3-iodocarbazole by the method described under the separation of 3-iodocarbazole and 3 : 6-di-iodocarbazole. Using theoretical quantities (2·9 g. of 3-iodocarbazole, 1·4 g. of benzoyl chloride, and 0·6 g. of solid

potassium hydroxide in 20 c.c. of acetone), the yield was practically as good. Twenty-five per cent. of the 3-iodocarbazole was recovered; (*b*) from 9-benzoylcarbazole—(i) 9-Benzoylcarbazole (4 g.), potassium iodide (1·6 g.) and potassium iodate (excess) in glacial acetic acid (40 c.c.) were boiled until the solution became colourless (1¼ hours). It was then decanted from unchanged iodate into water, and the salmon-pink, powdery solid recrystallised from acetone. The yield of pure 3-iodo-9-benzoylcarbazole was 2·2 g. A small amount, m. p. 201°, was obtained from the residues by crystallisation from pyridine. It is therefore probably 3 : 6-di-iodo-9-benzoylcarbazole: (ii) 9-Benzoylcarbazole (5·4 g.) and iodine (2·5 g.) were dissolved in glacial acetic acid (100 c.c.), and a solution of nitric acid in acetic acid was added as in the preparation of 3-iodo-9-acetylcarbazole. The solution became clear in about 20 minutes, was poured into water, and the precipitated yellow solid crystallised from pyridine with addition of a drop of water. The crystals so obtained dissolved in alcohol except a small amount of insoluble, white substance, which, after recrystallisation from pyridine, melted at 204—205° and was 3 : 6-di-iodo-9-benzoylcarbazole. The alcoholic filtrate therefrom deposited 3-iodo-9-benzoylcarbazole. It crystallised well from alcohol, but the crystals were ill-defined and resembled seaweed in shape and arrangement. On certain occasions when the alcoholic solutions were left standing, the crystals assumed a plate shape, but this could not be repeated at will. The acetone solution of 3-iodo-9-benzoylcarbazole deposited clusters of very long needles, which could be removed and were stable out of the solution, whereas the crystals remaining in solution, if scratched, immediately changed into thick, six-sided plates. The acetone solution usually deposited a mixture of needles and plates. Pyridine, in which it is very soluble, and light petroleum, in which it is soluble with difficulty, also gave plate crystals. It is sparingly soluble in glacial acetic acid, but crystallisation therefrom does not purify the substance. Benzene and carbon tetrachloride solutions gave small, colourless crystals. The two crystalline forms mentioned above melted at 145—146°, and a mixed m. p. was unchanged. The substance is therefore dimorphic. Exposure to light turns it faintly brown; a property possessed also by 9-benzoylcarbazole. It is readily hydrolysed to 3-iodocarbazole by alcoholic potassium hydroxide solution.

3 : 6-*Di-iodo-9-benzoylcarbazole.*—3 : 6-Di-iodocarbazole (1 g.) was treated with benzoyl chloride (0·6 g.) and potassium hydroxide (0·5 g.) in acetone (20 c.c.) in the usual way. 3 : 6-Di-iodo-9-benzoylcarbazole was precipitated, and after washing with hot acetone, in which 3 : 6-di-iodocarbazole is very soluble, was obtained

pure (0·8 g.), m. p. 204—205°. A mixed m. p. with 3 : 6-di-iodocarbazole (m. p. 202—204°) was much lower. It crystallises best from a dilute solution in pyridine, to which a few drops of water are subsequently added, in long rods. It is much less soluble in carbon tetrachloride, and soluble with difficulty in acetone, from which microcrystals are obtained. It is readily hydrolysed by alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

3-*Iodo*-9-*toluene*-p-*sulphonylcarbazole* was prepared thus: (i) 3-Iodocarbazole (1·5 g.), toluene-*p*-sulphonyl chloride (1·0 g.), and potassium hydroxide (0·3 g.) in acetone (10 c.c.) were boiled together for 10 minutes, and poured into water. The precipitated solid crystallised from alcohol, in which it was sparingly soluble, in colourless, diamond-shaped rhombs (1·3 g.), m. p. 170—171° (Found: I, 28·5. $C_{19}H_{14}O_2NIS$ requires I, 28·4%). 3-Iodocarbazole (0·3 g.) was recovered from the alcoholic filtrate. 3-Iodo-9-toluene-*p*-sulphonylcarbazole is easily soluble in cold pyridine, hot acetone, benzene, glacial acetic acid, ethyl acetate, aniline, or carbon tetrachloride, and less soluble in light petroleum, from all of which it crystallises, but best from acetone, benzene, alcohol–acetone, or alcohol–pyridine. (ii) 9-Toluene-*p*-sulphonylcarbazole * (2·6 g.) and iodine (0·8 g.) were dissolved in glacial acetic acid (50 c.c.), and a solution of nitric acid in glacial acetic acid (usual strength) was slowly added to the boiling solution. In 10 minutes, about 3 c.c. of the nitric acid solution had been added, and the solution was free from iodine coloration. The pale yellow solution poured into water gave a canary-yellow solid, which was extracted with alcohol. A white, insoluble portion crystallised from much glacial acetic acid in colourless needles, m. p. 257°. It is 3 : 6-*di-iodo*-9-*toluene*-p-*sulphonylcarbazole* (Found: I, 43·7. $C_{19}H_{13}O_2NI_2S$ requires I, 44·3%). The alcoholic extract deposited impure 3-iodo-9-toluene-*p*-sulphonylcarbazole, a substance melting at 175°, and colourless rods melting at 118—121° (Found: I, 11·4; *M*, by Rast's method, 334. A mixture of 9-toluene-*p*-sulphonylcarbazole and 3-iodo-9-toluene-*p*-sulphonylcarbazole, $C_{19}H_{15}O_2NS + C_{19}H_{14}O_2NIS$, requires I, 16·5%; *M*, 384).

(iii) 9-Toluene-*p*-sulphonylcarbazole (1 g.) was boiled with potassium iodide (0·34 g.) and excess of potassium iodate in glacial acetic acid (10 c.c.) for several hours, but the iodine coloration did not disappear. In another experiment, using half the quantity of

* Compare footnote on benzoylation of carbazole. Application of the same method of removal of carbazole after preparation of 9-toluene-*p*-sulphonylcarbazole produced the latter in large, colourless, prismatic crystals, softening at 128°, and giving a clear melt at 133° (compare Cassella, D.R.-P. 224951, 1909; Herz, A.P. 966092, 1910).

potassium iodide, the colour was discharged in 2¼ hours and a nearly theoretical yield of the substance (m. p. 118—121°) mentioned under (ii) was obtained.

3 : 6 - *Di* - *iodo* - 9 - *toluene* - p - *sulphonylcarbazole.* — 9-Toluene-*p*-sulphonylcarbazole (2·5 g.), iodine (2·0 g.), and glacial acetic acid (50 c.c.) were boiled together during addition of nitric acid in acetic acid (usual strength) until the iodine colour disappeared (45—60 minutes). Before the colour had vanished, needle-shaped crystals began to separate. The mixture was allowed to cool; the separated crystals crystallised from glacial acetic acid and then from benzene in tetrahedral prisms, m. p. 257°. It is only slightly soluble in glacial acetic acid, carbon tetrachloride or acetone, but readily soluble in hot benzene.

Iodination of 9-*Methylcarbazole.*—The methylation of 3-iodocarbazole has been described (Stevens and Tucker, *loc. cit.*, 2146). Iodination of 9-methylcarbazole was effected as follows: 9-Methylcarbazole (0·8 g.), potassium iodide (0·47 g.), and excess of potassium iodate were boiled in glacial acetic acid (10 c.c.) for 2 minutes, in which time a green solution was obtained. By the usual treatment there were separated in small quantity by means of alcohol 3-iodo-9-methylcarbazole and a product, m. p. 181°. The latter is 3 : 6-*di-iodo*-9-*methylcarbazole* (Found: I, 58·6. $C_{13}H_9NI_2$ requires I, 58·7%). It was also prepared by the action of methyl sulphate on 3 : 6-di-iodocarbazole in presence of acetone and solid potassium hydroxide. It is readily soluble in glacial acetic acid, very sparingly soluble in alcohol, and, although sparingly soluble, crystallises from acetone in long, thin rods, m. p. 181—182°.

Iodination of 9-*Ethylcarbazole.*—9-Ethylcarbazole (19·5 g.) and potassium iodide (11·0 g.) were dissolved in glacial acetic acid (200 c.c.), and potassium iodate (16 g.) was added in portions to the hot solution. A gentle reaction set in, and the colour soon gave place to green. The solution was poured into water, and a pasty solid possessing a silky sheen was deposited. This was dissolved in excess of glacial acetic acid. In sufficiently dilute solution, no oil separated, but impure green crystals (11 g.), m. p. 71°. The filtrate from these on concentration deposited colourless crystals, m. p. 80° (3·5 g.). By further concentration, a final crop (5·5 g.) of green crystals, m. p. 140—144°, was obtained. The crystals, m. p. 80°, were purified by recrystallisation from glacial acetic acid or alcohol, and separated in long needles, m. p. 83—84°, identical with 3-iodo-9-ethylcarbazole (Stevens and Tucker, *loc. cit.*). The green crystals, m. p. 140—144°, crystallised from much glacial acetic acid and finally from alcohol in colourless needles, m. p. 152—153°, and were shown to be 3 : 6-*di-iodo*-9-*ethylcarbazole* (Found:

I, 56·9. $C_{14}H_{11}NI_2$ requires I, 56·8%). It is only slightly soluble in alcohol or in glacial acetic acid.

3-*Iodo*-9-iso*propylcarbazole* was prepared by Mr. W. H. Chalmers, B.Sc., A.I.C., by boiling a mixture of 3-iodocarbazole (2 g.), *iso*propyl iodide (4 g.), and potassium hydroxide (2 g. in 1 c.c. of water) in acetone (6 c.c.) for 6 hours. The usual procedure, and crystallisation of the product from glacial acetic acid, gave white, silvery leaflets, m. p. 95—97° (Found: I, 38·2. $C_{15}H_{14}NI$ requires I, 37·9%).

3-*Iodocarbazole* could not be obtained from carbazole by the action of iodine and nitric acid in glacial acetic acid. It crystallises well from light petroleum, and is very soluble in benzene, pyridine, or acetone. As already stated, it is best crystallised from carbon tetrachloride or glacial acetic acid.

3 : 6-*Di-iodocarbazole*, isolated in small yield in the iodination of carbazole, was prepared from carbazole by method (i), using twice the quantity of potassium iodide used to obtain monoiodocarbazole, and proceeding as before. Purification of the pink product was difficult, but it was effected as given under the mercuric oxide experiment, method (ii). It was found best, in order to obtain pure 3 : 6-di-iodocarbazole, to acetylate or benzoylate the material (as described above), and hydrolyse the product with alcoholic potassium hydroxide solution. 3 : 6-Di-iodocarbazole is very soluble in acetone. It crystallises best from glacial acetic acid or alcohol, in long laminæ.

UNIVERSITY OF GLASGOW. [*Received, November* 13*th*, 1925.]

LXXV.—*Optical Activity and the Polarity of Substituent Groups. Part III. Menthyl Acetophenone-o-carboxylate.*

By HAROLD GORDON RULE and JOHN SMITH.

IN certain cases it has now been established that the influence of substituents on the optical rotatory power of an organic compound is similar to their influence on acidity. This has been shown to hold true for the condensation products of an optically active base with substituted benzaldehydes (Betti, *Gazzetta*, 1923, **53**, 417) and for the menthyl esters of monosubstituted acetic acids (Rule and Smith, J., 1925, **127**, 2188).

On the other hand, the menthyl esters of substituted benzoic acids prepared by Cohen reveal an influence of a quite different type. Here the relative changes in rotation produced by a number of simple

ortho-substituents (substitution in the *m*- or *p*-position has little effect) are given by $NO_2 > CO_2H > H > I > CH_3 > Br > Cl > F > O{\cdot}CH_3$. As has already been pointed out (Rule, J., 1924, **125**, 1122; Rule and Paterson, *ibid.*, 2159), this series is in very close agreement with the relative polarity of the groups as deduced from the molecular inductive capacities of compounds, and with the relative effect of the substituents on the nitration of benzene as we pass from the strongly positive (meta-directive) nitro-group to the strongly negative (para-directive) fluoro-group.

Only two positive groups occur in the above series and, unfortunately, few other simple groups of this type can be readily tested in the case of the menthyl benzoates. Acetophenone-*o*-carboxylic acid, however, is a comparatively accessible compound and figures are available relating to the influence of the acetyl group on benzene substitution.

It has been shown by Camps (compare Holleman, "Die direkte Einführung von Substituenten," 1910, p. 190) that when acetophenone is nitrated at 15° it yields a mixture of about 55% of the *m*-compound and 45% of the *o*-compound. Comparing these figures with those previously quoted for the nitration of nitrobenzene and of benzoic acid (Rule and Paterson, *loc. cit.*), we obtain:

	NO_2.	CO_2H.	$CO{\cdot}CH_3$.
m-Compound.	93	76	55%

The determination of the relative polarity of the acetyl group from molecular inductive capacity data is inconclusive, as will be seen from the following values (X = $CH_3{\cdot}CO$):

Series.		Dielec. const.	Density.	Mol. ind. capac.
HX.	Acetaldehyde.	18·5	0·80	10·1
EtX.	Methyl ethyl ketone.	17·8	0·81	15·8
C_6H_5X.	Acetophenone.	18·1	1·03	21·0

On comparing these figures with those calculated by Rule and Paterson (*loc. cit.*), it is found that the *m*-directive groups fall into the order:

Series	HX.	—	CN,	CO_2H,	$CO{\cdot}CH_3$,	H.
	EtX.	NO_2,	CN,	$CO{\cdot}CH_3$,	CO_2H,	H.
	C_6H_5X.	NO_2,	CN,	$CO{\cdot}CH_3$,	CO_2H,	H.

From the evidence of the benzene substitution data, which is partly supported by that of inductive capacity, it may be concluded that the acetyl group falls between the carboxyl group and hydrogen.

The menthyl ester of acetophenone-*o*-carboxylic acid has now been prepared, and the optical properties of the compound have been

examined for sodium light and that of the three chief mercury lines. Owing to the slight yellow colour of the melt, the rotation of the fused ester could only be determined over the range λ_D to λ_{gr}, but the rotatory power in benzene and in acetone solution was examined over the range λ_D to λ_{vi}. The values of $1/\alpha$ when plotted against λ^2 gave straight lines. In addition, the dispersion ratio α_{gr}/α_D for the fused ester at 94° and for solutions in benzene and acetone at the ordinary temperature remained approximately constant in the neighbourhood of 1·213. It may therefore be concluded that the compound exhibits normal and apparently simple rotatory dispersion in this region of the spectrum. The molecular rotations were as follows: fused ester, $[M]_D^{94°} = -261°$; in benzene (5%), $[M]_D^{20°} = -284°$; in alcohol (2%), $[M]_D^{19·5°} = -267°$; in acetone (5%), $[M]_D^{18·8°} = -253°$.

Like other positive *o*-substituents, the acetyl group therefore brings about an increase in the rotation of menthyl benzoate. The influence of various *o*-substituents in this case is summarised in the following table, in which the additional figures for the molecular rotations were determined by Cohen and those for the dispersion ratios by Pickard and Kenyon:

Substit.	NO_2.	CO_2H.	$CO{\cdot}CH_3$.	H.	I.	CH_3.	Br.	Cl.	F.	$O{\cdot}CH_3$.
$[M]_D$	−381*	332†	261‡	239	237	231	205	195	194	148
α_{gr}/α_D	1·26	1·21	1·21	1·18	1·19	—	—	—	1·18	—

* At 65°. † In solution. ‡ At 94°.

The remarkably close correspondence between the effect of substituents on the rotatory power of menthyl benzoate (I) and on benzene substitution (II) is seen by a comparison of the series given below, in which the agreement is broken only by a slight displacement of the iodine atom. Series III represents the relative polarity of the substituents as determined from the inductive capacities of compounds.

I. $NO_2 > CO_2H > CO{\cdot}CH_3 > H > I > CH_3 > Br > Cl > F > O{\cdot}CH_3$
II. NO_2, CO_2H, $CO{\cdot}CH_3$, H, CH_3, Br, I, Cl, F
III. NO_2, CO_2H (?), $CO{\cdot}CH_3$, CO_2H (?), H, CH_3, I, Br, Cl, F.

Experimental.

Acetophenone-*o*-carboxylic acid was prepared by the method of Gabriel and Neumann (*Ber.*, 1893, **26**, 952). Phthalic anhydride, acetic anhydride, and potassium acetate were heated together to give phthalylacetic acid, and the latter, after purification, was converted into acetophenone-*o*-carboxylic acid by heating under pressure with water at 200°. After several recrystallisations from

water, the acid melted sharply at 112° (Gabriel and Michael, *Ber.*, 1877, **10**, 1554, quote 114—115°).

Menthyl acetophenone-o-carboxylate was prepared from the above acid by esterification in the presence of dry hydrogen chloride. The crude ester was freed from most of the excess menthol by heating at 200° under 10 mm. pressure, and was recrystallised from light petroleum until of constant rotation. The pure compound separated in colourless, odourless crystals, m. p. 92° (Found: C, 75·4; H, 8·6. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

The compound dissolves comparatively readily in benzene, but is not very soluble in other organic solvents at the ordinary temperature.

The following figures refer to the rotatory power of the ester in the fused state at 94°. All rotations were measured in a 50 mm. tube and were negative in sign. $D_4^{94°} = 0{\cdot}9898$ (α_{vl} could not be determined owing to the slight yellow tint of the liquid).

a_D.	a_{ye}.	a_{gr}.	a_{gr}/a_D.	$[a]_D$.	$[a]_{ye}$.	$[a]_{gr}$.	$[M]_D$.
42·84	45·04	51·98	1·213	86·56	91·01	105·0	261·4

In addition, a number of measurements were made of the rotatory power in solution at about 20°. In each case the highest concentration quoted represents the maximum at which it is convenient to work, and is not far removed from the saturation point. All rotations are negative in sign.

Solvent.	G. of ester in 100 c.c.	a obs.	($l = 2$).	$[a]_\lambda$.	a_{gr}/a_D.	$[M]_D$.
Benzene (20°).	5·000	a_D	9·42	94·2	1·216	284·5
		a_{ye}	9·90	99·0		
		a_{gr}	11·46	114·6		
		a_{vl}	22·03	220·3		
Benzene (20·1°).	20·010	a_D	37·68	94·15	1·211	284·3
		a_{gr}	45·60	113·9		
Acetone (18·8°).	5·054	a_D	8·48	83·9	1·211	253·4
		a_{ye}	8·90	88·1		
		a_{gr}	10·26	101·5		
		a_{vl}	18·85	186·5		
Alcohol (19·5°).	2·001	a_D	3·54	88·46		267·0

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UNIVERSITY OF EDINBURGH. [*Received, November 24th*, 1925.]

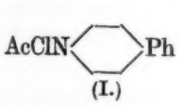
LXXVI.—*The Chlorination and Bromination of 4-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

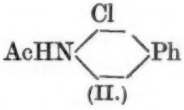
THE action of chlorine or bromine on 4-aminodiphenyl and on its acetyl derivative appears to have been investigated in only one instance, where it was shown that, by direct bromination of 4-acetylaminodiphenyl, 4′-bromo-4-acetylaminodiphenyl resulted (Hübner, *Annalen*, 1881, **209**, 339). Other halogen derivatives, however, have been prepared from benzidine and from tolidine by an adaptation of the Sandmeyer reaction (Taüber, *Ber.*, 1894, **27**, 2627; Gelmo, *Ber.*, 1906, **39**, 4175); the structure of these compounds necessarily follows from their method of preparation.

The present investigation had as its objects the preparation of the *N*-halogen derivatives and their conversion into ring-substituted products; and the direct introduction of chlorine or bromine into the molecule of 4-aminodiphenyl or 4-acetylaminodiphenyl.

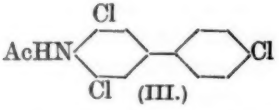
It was found that a stable *N*-chloro-4-acetylaminodiphenyl (I) could be obtained from which 3-chloro-4-acetylaminodiphenyl (II) resulted; the latter compound again could be converted into a *N*-chloro-derivative which was unstable, lost chlorine, and from which a ring-substituted product could not be obtained. The corresponding *N*-bromo-4-acetylaminodiphenyl could be prepared only in an impure state, it lost bromine with ease, and the original acetyl derivative was not recovered.



(I.)



(II.)



(III.)

The chlorination of the free base was attempted under various conditions, but only deeply coloured and tarry products were obtained. In contrast to this, the acetylated base could be substituted readily with the formation of 3-chloro-4-acetylaminodiphenyl, and on further chlorination 3 : 5 : 4′-trichloro-4-acetylaminodiphenyl (III) was obtained. It was found impossible to introduce more than these three atoms of chlorine into the molecule and obtain a product capable of being separated into individual compounds.

The bromination of the free base proceeded smoothly, yielding 3 : 5-dibromo-4-aminodiphenyl, and under altered conditions the latter compound could be further brominated to give 3 : 5 : 4′-tribromo-4-aminodiphenyl. Higher bromination products appear

to be formed; but from the mixture of substances produced it has been found impossible, so far, to isolate individual compounds. The acetyl derivative of the base on bromination yielded either 4′-bromo-4-aminodiphenyl or its acetyl derivative and a small quantity of a dibrominated product which has been shown to be 3 : 4′-dibromo-4-acetylaminodiphenyl. Bromination at a higher temperature yielded 3 : 5 : 4′-tribromo-4-aminodiphenyl.

The orientation of substituents in the nuclei of diphenyl is of a complex nature; thus whilst 4-aminodiphenyl and its acetyl derivative on chlorination or nitration yield a product substituted in the position adjacent to the amino-group, yet when the substituent in the 4-position is varied as widely as the halogens, the nitro-group and the carboxyl group the entering substituent goes to the 4′-position.

As the direct substitution of only 2- and 4-monosubstituted diphenyl derivatives has been investigated, it is impossible to put forward more than tentative suggestions. The following assumptions appear to be necessary :

(*a*) The usual directive influence is to be ascribed to all the simple groups.

(*b*) The phenyl group and the group C_6H_4X (where X may be an ortho-para or meta-directing group) have a strong ortho-para-directive influence.

(*c*) The amino-, hydroxy-, and derived groups promote substitution in the same nucleus.

Thus it appears that the position taken up by a substituent depends on the velocity with which substitution can be effected. This is in agreement with the experimental evidence that ortho-para-directing groups, and in particular the amino- or hydroxy-group, render substitution easy, whereas meta-directing groups tend to make substitution a comparatively slow process.

Alternatively, it might be suggested that substitution only occurs in the nucleus containing the directing group when this group is capable of being itself substituted and then undergoing a rearrangement which transfers the substituent to the ring. This would be in accord with the behaviour of amino- and hydroxy-groups.

The behaviour of 4-acetylaminodiphenyl on monobromination is very striking, since it appears to be the only known case among the substitution products of 4-amino- or 4-hydroxy-diphenyl in which the first substituent enters the 4′-position; this result is still more unexpected, since 4-aminodiphenyl itself gives rise to a normal sequence of substitution products.

This abnormal behaviour might be ascribed to (*a*) a mechanism for this bromination different from that involved in all other cases, or (*b*) steric influences. Three alternative mechanisms appear

possible: (1) the formation of a *N*-halogen compound followed by an *intra*molecular change; (2) the formation of a *N*-halogen compound followed by an *inter*molecular change; and (3) the direct interaction of the halogen and the aminodiphenyl molecules. Since *N*-bromo-4-acetylaminodiphenyl cannot be converted into a ring-substituted product, mechanism (1) cannot be the mechanism involved; since the corresponding *N*-chloro-compound can be thus transformed and since direct chlorination yields the same product, any one of the three mechanisms may be involved.

To ascribe the difference in behaviour to a steric factor would imply that by acetylation of the base the velocity of interaction of bromine with the more reactive hydrogen atoms in the 3- and 5-positions is decreased to such an extent that the less reactive hydrogen atom in the 4′-position is substituted almost exclusively.

It is the intention of the authors to complete a study of the chlorination and bromination of 2-aminodiphenyl and to extend the work to a consideration of 3-nitro- and 3-amino-diphenyl.

Experimental.

4-Aminodiphenyl was prepared by nitrating diphenyl by Ludens's method (*Ber.*, 1875, **8**, 871) and reducing the product by Schlenk's method (*Annalen*, 1909, **368**, 303).

N-Chloro-4-acetylaminodiphenyl.—To a suspension of 10·6 g. of 4-acetylaminodiphenyl in a solution of 13 g. of sodium bicarbonate in 200 c.c. of water, 150 c.c. of *N*-sodium hypochlorite were added during 2 hours. The product was collected after 12 hours, washed with water, dried, and extracted with light petroleum (b. p. 40—60°), in which 4-acetylaminodiphenyl is insoluble. The *chloroamine* crystallised from carbon tetrachloride in colourless needles, m. p. 129·5° (Found: Cl, 14·3. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

3-Chloro-4-acetylaminodiphenyl.—(a) *Conversion of the chloroamine.* To a hot solution of 5 g. of the chloroamine in 100 c.c. of spirit and 2—3 c.c. of glacial acetic acid, sufficient water was added to start precipitation. The product separated on cooling, and crystallised from dilute alcohol in needles, m. p. 147°.

(b) *Direct chlorination of 4-acetylaminodiphenyl.* Chlorine was passed into a 2% solution of the acetylamine in glacial acetic acid, cooled in ice-water, until the theoretical gain in weight was obtained. The product, which was precipitated with water, contained higher chlorination products (Found: Cl, 14·7. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

3-Chloro-4-aminodiphenyl hydrochloride was obtained on hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid. The

salt separated from the solution, on cooling, in long needles, m. p. 217° (decomp.) (Found : HCl, 15·1. $C_{12}H_{10}NCl$,HCl requires HCl, 15·2%).

3-*Chloro*-4-*aminodiphenyl* was precipitated from the solution of the hydrochloride by dilute ammonia. It crystallised from dilute alcohol in needles, m. p. 71° (Found : Cl, 17·2. $C_{12}H_{10}NCl$ requires Cl, 17·4%).

3 : 4-*Dichlorodiphenyl*, obtained from the amine by the usual methods, was a faintly yellow oil, b. p. 195—200°/15 mm., which solidified to a pale yellow, crystalline mass, m. p. 46° (Found : Cl, 30·8. $C_{12}H_8Cl_2$ requires Cl, 31·8%). On oxidation of this crude product with chromic anhydride in glacial acetic acid solution, 3 : 4-dichlorobenzoic acid was obtained (m. p. 200°).

3-*Chloro*-4-*acetylchloroaminodiphenyl*.—The chloroamine was prepared in the manner described for 4-acetylchloroaminodiphenyl. It was a white powder soluble in non-aqueous solvents; it could not be obtained pure owing to the ease with which it lost chlorine. Several attempts were made, under various conditions, to bring about a rearrangement, but in each case chlorine was evolved and 3-chloro-4-acetylaminodiphenyl was obtained.

3 : 5 : 4′-*Trichloro*-4-*acetylaminodiphenyl*.—Chlorine and carbon dioxide were passed slowly into a 5% solution of 4-acetylaminodiphenyl, the temperature being kept as low as possible. Excess chlorine was removed with a current of air, and the solution diluted with water until precipitation commenced. The product crystallised from acetone in needles, m. p. 236° (Found : Cl, 33·6. $C_{14}H_{10}ONCl_3$ requires Cl, 33·8%).

3 : 5 : 4′-*Trichloro*-4-*aminodiphenyl*.—The acetyl derivative was hydrolysed with alcoholic hydrochloric acid; the *amine*, which separated from the solution in long needles, was recrystallised from alcohol; m. p. 128° (Found : Cl, 38·9. $C_{12}H_8NCl_3$ requires Cl, 39·05%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-chlorobenzoic acid was obtained (m. p. 235°).

N-*Bromo*-4-*acetylaminodiphenyl* was obtained as was the corresponding chloro-compound. It was a pale yellow powder, easily soluble in non-aqueous solvents, and lost bromine very easily. As it could not be obtained pure, it was not further investigated.

4′-*Bromo*-4-*aminodiphenyl*.—To a well-cooled 10% solution of 4-acetylaminodiphenyl in glacial acetic acid was added slightly more than 1 mol. of bromine. After 24 hours, on pouring into water, a mixture of brominated products was obtained which, by fractional crystallisation from dilute acetic acid, was separated into a more soluble monobromo-derivative and a less easily soluble dibromo-derivative. The former was 4′-bromo-4-aminodiphenyl and not its

acetyl derivative (compare Hübner, *loc. cit.*). It crystallised from dilute acetic acid in long needles, m. p. 145° (Found : Br. 32·2. $C_{12}H_{10}NBr$ requires Br, 32·1%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-bromobenzoic acid was obtained (m. p. 251°).

3 : 4′-*Dibromo*-4-*acetylaminodiphenyl*.—The less soluble dibromo-derivative crystallised from acetone in colourless needles, m. p. 197° (Found : Br, 43·25. $C_{14}H_{11}ONBr_2$ requires Br, 43·4%). The acetyl derivative was hydrolysed with alcoholic hydrobromic acid. The free base was not purified and analysed, as only a very small quantity was available; but was converted directly into a tribromo-derivative by bromination in glacial acetic acid solution. The product was crystallised from acetone and then from dilute acetic acid; it had m. p. 148°, alone or mixed with 3 : 5 : 4′-tribromo-4-aminodiphenyl. The original acetyl derivative was not identical with 3 : 5-dibromo-4-acetylaminodiphenyl, whence it follows that the acetyl derivative must have the bromine atoms in the 3- and 4′-positions.

3 : 5-*Dibromo*-4-*aminodiphenyl*.—The calculated quantity of a 10% solution of bromine in glacial acetic acid was added to a cold glacial acetic acid solution of 4-aminodiphenyl. The yellow precipitate was filtered off and washed with dilute sodium carbonate solution. It crystallised from alcohol in colourless needles, m. p. 119° (Found : C, 44·1; H, 2·9; Br, 48·8. $C_{12}H_9NBr_2$ requires C, 44·05; H, 2·8; Br, 48·9%).

3 : 5-*Dibromo*-4-*acetylaminodiphenyl* was prepared by heating the base with acetic anhydride in glacial acetic acid solution. After crystallising from alcohol, it melted at 162° (Found : Br, 43·45. $C_{14}H_{11}ONBr_2$ requires Br, 43·4%).

3 : 5-*Dibromodiphenyl*, obtained from the base by elimination of the amino-group in the usual manner, was a pale yellow oil, b. p. 208°/15 mm., m. p. 15° (Found : Br, 51·3. $C_{12}H_8Br_2$ requires Br, 51·3%). On oxidation with chromic anhydride in glacial acetic acid solution in a sealed tube at 200° 3 : 5-dibromobenzoic acid was obtained (m. p. 212°).

3 : 5 : 4′-*Tribromo*-4-*aminodiphenyl*.—Bromine (1 mol.) was added to a boiling solution of 3 : 5-dibromo-4-aminodiphenyl in glacial acetic acid, and the mixture refluxed until the colour of the bromine had disappeared (usually about 45 minutes). The product precipitated by addition of water crystallised from dilute acetone in white needles, m. p. 149°. The same substance was obtained by direct bromination of 4-acetylaminodiphenyl in boiling glacial acetic acid (Found : C, 35·4; H, 2·0; Br, 59·0. $C_{12}H_8NBr_3$ requires C, 35·4; H, 2·2; Br, 59·0%). On oxidation with chromic anhydride

in glacial acetic acid solution *p*-bromobenzoic acid was obtained (m. p. 251°).

The *acetyl* derivative crystallised from acetone in white needles, m. p. 256° (Found: Br, 53·5. $C_{14}H_{10}ONBr_3$ requires Br, 53·6%).

All m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid was established by the " mixed m. p. " method.

The authors wish to express their thanks to Dr. H. McCombie for the interest he has taken in the work. One of them (W. A. W.) is indebted to the Master and Fellows of Gonville and Caius College for a studentship which enabled him to collaborate in this work.

UNIVERSITY CHEMICAL LABORATORIES,
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LXXVII.—*The Influence of the Intensity of Illumination on the Velocity of Photochemical Changes. The Determination of the Mean Life of a Hypothetical Catalyst.*

By FRANK BRIERS, DAVID LEONARD CHAPMAN, and ERNEST WALTERS.

ONLY a few researches have been conducted on the variation of the rates of photochemical changes with the intensity of the light, and at present there is some degree of discordance in the conclusions drawn by different experimenters from the results of their experiments.

Draper (*Phil. Mag.*, 1843, **23**, 401) announced that the rate at which chlorine and hydrogen combine in light is proportional to the intensity of the illumination. Baly and Barker (J., 1921, **119**, 653) maintained that the ratio of the rate of union of the two gases to the intensity of the light increases as the intensity of the light is increased. M. C. C. Chapman (J., 1924, **125**, 1521) obtained a result in substantial agreement with that of Draper. She found, however, that as the intensity of the radiation is increased the rate of formation of hydrochloric acid increases in a slightly smaller ratio. Berthoud (*Helv. Chim. Acta*, 1924, **7**, 324) considered that the rate of union of chlorine and hydrogen in the absence of inhibitors would be proportional to the square root of the intensity of illumination, and he saw in some of Mrs. Chapman's results evidence that such is the case. Kornfeld and Müller (private communication from Professor Bodenstein) have confirmed Mrs. Chapman's results. They find

that the rate of formation of hydrochloric acid is proportional to the intensity of the light when the intensity is varied in the ratio of 1 : 64.

Draper, Baly and Barker, and Mrs. Chapman used electrolytic gas, which always contains a small amount of oxygen. Kornfeld and Müller removed oxygen from the hydrogen; but the chlorine they used may have contained a little oxygen.

It is possible that Berthoud's contention is right. The electrolytic gas used by Mrs. Chapman undoubtedly contained a little oxygen, and the small deviations from proportionality observed by her were in the direction required by Berthoud's view.

In a recent paper by Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) on the photochemical synthesis of hydrobromic acid it is concluded that the rate of formation of this compound from its elements is directly proportional to the square root of the intensity of the light. The striking difference, in this particular, of the influence of light on mixtures of bromine with hydrogen and of chlorine with hydrogen may possibly be due to the effect of small quantities of oxygen on the photochemical union of the latter gases. The question needs to be submitted to further investigation.

In connexion with the subject of this communication, the reaction between iodine and potassium oxalate is of especial interest. This reaction is represented by the equation:

$$C_2O_4K_2 + I_2 = 2CO_2 + 2KI.$$

It has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **16**, 1097; *Ann. Chim.*, 1919, **11**, 130; J., 1923, **123**, 1856) and by Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307). In his first paper, Dhar maintained that the velocity of the action is proportional to the intensity of the light. On the other hand, Berthoud and Bellenot asserted that it is proportional to the square root of the intensity of the light, both for red and for blue light. In order to vary the intensity of the light the latter investigators inserted between the source of illumination and the solution a large disc of black cardboard which could be set in rapid rotation, and from which two equal sectors had been removed for the first series of measurements; four for a second series, and eight for a third series, so as to make the intensity vary in the ratios 1 : 2 : 4. They realised that this method of varying the intensity of the light would not be legitimate unless the duration of the secondary reactions considerably exceeded the intervals between successive illuminations, and they deduced that if this condition were fulfilled the velocity of reaction ought to diminish as the rate of rotation of

the disc is reduced. They observed the anticipated falling off in the velocity of the reaction, but they were unable to obtain the theoretical result when the disc was rotating very slowly.

We have repeated the experiments of Dhar and of Berthoud and Bellenot, and our results agree with those of the latter researchers. We have also examined more closely the theory of the effect of intermittent illumination on photochemical reactions of the same class, and have drawn conclusions from the theory and from our experimental results which will be given below.

The reaction between potassium oxalate and iodine, according to Berthoud and Bellenot, is of the same class as that between chlorine and hydrogen. One quantum of absorbed light is sufficient to cause the interaction of a large number of molecules of the reacting substances. For the explanation of such reactions several special hypotheses have been proposed. These hypotheses have one feature in common in that they postulate the formation of an unstable catalyst (or chain of catalysts) by the direct action of the light. We shall make no special assumption concerning the nature of the catalyst, but we shall assume that:

(I) the rate of formation of the catalyst is proportional to the intensity of illumination;

(II) the rate of reaction is proportional to the concentration of the catalyst; and

(III) the rate of destruction of the catalyst is proportional to a power of its concentration.

If [A] represents the concentration of the catalyst and I the intensity of the light, we have from assumptions I and III

$$d[\mathrm{A}]/dt = cI - k[\mathrm{A}]^n$$
$$= 0 \text{ in the steady state,}$$

and therefore in the steady state

$$I^{1/n} \propto [\mathrm{A}] \propto \text{the rate of reaction (from assumption II).}$$

Therefore in the case of the formation of hydrochloric acid from electrolytic gas $n = 1$ if the experiments of Mrs. Chapman and of G. Kornfeld and H. Müller are trustworthy, whereas in the case of the interaction of iodine and potassium oxalate $n = 2$ if the observations of Berthoud and Bellenot and of the authors are not subject to some unsuspected source of error.

We have spent 6 months in attempts to discover some explanation of Berthoud and Bellenot's results other than that given by the authors, namely, that in this reaction the velocity of change is not proportional to the intensity of illumination but to its square

root, and we have satisfied ourselves that none of the following causes could furnish such an explanation:

(1) The presence of an inhibitor.

(2) The varying rates of escape of the carbon dioxide produced in the reaction.

(3) The more rapid removal of the iodine from that portion of the solution which is nearest to the light.

(4) The method employed for varying the intensity of the light.*

When the method of varying the intensity of the light was that of a rotating disc, consistent and reproducible results in agreement with those of Berthoud and Bellenot were obtained. The results were independent of the rate of rotation of the disc when this rate exceeded one thousand revolutions per minute. It must therefore be concluded that when the solution has been exposed to light the chemical action continues for some time after the light has been shut off: for otherwise the rate of chemical change would be

* That inhibitors were not present was proved by the fact that the velocity of the reaction was not affected by the purification of the materials used (*i.e.*, by the fractional crystallisation of the potassium oxalate or by the sublimation of the iodine), the results being reproducible and, within reasonable limits, independent of the degree of purity of the reagents. Variation of the hydrogen-ion concentration had very little effect.

That the dissolved carbon dioxide had no effect was proved by the fact that the total amount of change in a given time, employing a constant intensity of light, was the same when the exposure was continuous and when it was intermittent, provided that the intervals of exposure were not too short.

Another method employed for varying the intensity of the light was the following. Two one thousand-watt lamps, A and B, were placed side by side so as to be symmetrically situated with respect to the reaction tube, which was contained in a thermostat. The currents passed through the lamps were separately adjusted so that each lamp emitted light of the sane intensity. The reaction vessel was exposed for 4 hours to the light emitted by A alone, and then for 4 hours to the light emitted by B alone. The change was measured, and compared with that effected in half the time by an exposure of the reaction vessel, filled with a solution of the same composition, to the light emitted simultaneously by both lamps. The mean ratio of the change effected by the light from one lamp in 8 hours to that effected by the light from two lamps in 4 hours was 1·32 : 1, the theoretical result calculated on the assumption that the rate of change is proportional to the square root of the intensity of the light being 1·41 : 1. The fact that the theoretical ratio was greater than that found experimentally can be explained by the circumstance that the large size of the bulbs of the two lamps made it impossible to place their filaments close together. That the effect of this source of error would be in the direction stated can be seen immediately by considering the effect of placing the lamps on opposite sides of the comparatively strongly absorptive solution.

proportional to the number of sectors left open in the disc, and not to the square root of this number. In other words, the catalyst assumed above has a life of appreciable duration.

Determination of the Life of the Catalyst or Chain.—The rate of disappearance of the catalyst is given by $k[A]^2$ and therefore in the steady state the mean life of the catalyst is

$$[A]/k[A]^2 = 1/k[A].$$

The problem is therefore to determine the value of $k[A]$ when the solution is exposed to light of a given intensity and has reached the steady state.

In the light

$$d[A]/dt = cI - k[A]^2.$$

Multiply both sides of the equation by k and put $ckI = a^2$ and $k[A] = x$.

The equation becomes

$$dx/dt = a^2 - x^2.$$

Or putting τ for at, and y for x/a,

$$dy/d\tau = 1 - y^2$$

the solution of which is

$$\int_{y_1}^{y_2}\left[\log_e \frac{1+y}{1-y}\right] = 2\tau_2 - 2\tau_1 \quad . \quad . \quad . \quad . \quad (1)$$

y is the ratio of $k[A]$ at the moment under consideration to its value in the steady state when the intensity of the light is I, and τ is the ratio of the time, t, to the duration of a mean life.

The differential equation which holds in the dark is

$$d[A]/dt = -k[A],^2$$

and its solution in terms of the variable y and τ is

$$\frac{1}{y_3} - \frac{1}{y_2} = \tau_3 - \tau_2 \, . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which y_3 and y_2 are the final and initial values of y, and τ_3 and τ_2 the corresponding values of τ.

In our experiments, the disc has eight sectors, each of angle $\pi/8$, symmetrically situated. Accordingly, when the disc was rotating uniformly, the duration of illumination was equal to the time during which the light was shut off, *i.e.*, $\tau_2 - \tau_1 = \tau_3 - \tau_2$. Also under the same conditions y_1 must attain a steady value which must be equal to y_3. Therefore from (1) and (2)

$$\log_e \frac{1+y_2}{1-y_2} + \frac{2}{y_2} = \log_e \frac{1+y_1}{1-y_1} + \frac{2}{y_1}.$$

For each value of y_1 the corresponding value of y_2 can be obtained from the above equation.

Moreover, if the value of τ is selected such that when $y = 0$ $\tau = 0$, equation (1) becomes

$$\log_e \frac{1+y}{1-y} = 2\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for each value of y there is a corresponding value of τ.

We shall now find the mean value of y for a given rate of rotation of the disc. From (3) the value of y during illumination is given by

$$y = \tanh \tau$$

and from (2) the value of y during the period of non-illumination is given by

$$y = 1/\left(\tau + \frac{1}{y_2}\right)$$

in which τ is the time (taking the mean life as the unit) during which the solution is in the dark and y_2 is the value of y when the light is shut off.

The mean value of y during uniform rotation of the disc is manifestly given by

$$y = \frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log\left[(\tau_2 - \tau_1)y_2 + 1\right]}{2(\tau_2 - \tau_1)}$$

But the mean value of y when the disc is rotating very rapidly is $1/\sqrt{2}$. Consequently, since the mean value of y is proportional to the rate of chemical change,

$$\frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log\left[(\tau_2 - \tau_1)y_2 + 1\right]}{\sqrt{2}(\tau_2 - \tau_1)} = \frac{\text{rate of change when the disc rotates at the given rate}}{\text{rate of change when the disc rotates very rapidly}}.$$

By trial a value of τ_1 is found which satisfies this equation. This can be done, since for every value of τ_1 there are corresponding values of τ_2 and y_2. Furthermore, as $\tau_2 - \tau_1$ is the duration of the exposure to light in mean lives, the value of the mean life can be calculated from the known rate of rotation of the disc.

Experimental.

The composition of the solution was potassium oxalate $N/2$, iodine $0{\cdot}00625N$, and potassium iodide $0{\cdot}00931N$. The reaction vessel was a glass cylinder of 4 cm. diameter, and it contained 80 c.c. of the above solution. The cylinder was closed with a ground glass stopper in order to prevent loss of iodine by evaporation, and during an experiment it was maintained at a temperature of 20°

in a thermostat filled with water and having sides of plane glass. A black screen was placed behind the reaction tube and the thermostat was covered so that no light could enter it except that which had passed through a sector of the disc and a window of the same shape as the sector in one of the glass sides of the thermostat. The reaction tube was placed near to the window in such a position that the whole of the solution it contained was equally illuminated. The source of light was a thousand-watt incandescent lamp placed at a horizontal distance of 38 cm. from the reaction vessel. The light from the lamp passed through an aperture of an appropriate shape in a large piece of cardboard which was placed immediately in front of the lamp, the aperture being of such a size that its penumbra was outside the window of the thermostat. The rotating disc was as near as possible to the thermostat and the reaction vessel. The shadow cast by the edge of the sector was quite sharp, but there was some error which could neither be avoided nor estimated, occasioned by reflexion from the inner wall of the glass bulb of the lamp. The lamp itself was, of course, placed in such a position that its incandescent wire subtended in a plane at right angles to the top edge of the window the minimum angle at a point in the solution. The disc was kept in rotation by means of a geared motor, and in some of the experiments in which the rotation was slow by a clock. The rates of chemical change were determined by finding the times required to bring about the same amount of chemical change as estimated by titration of the iodine with a standard solution of sodium thiosulphate. The mean life of the catalyst was in the first place determined when the solution was illuminated with white light. The results are recorded below:

A.	B.	C.	D.
20	71·75		
20	71·44		
Very fast	62·21	0·0303	0·000688
,,	62·20		
24	71·12		
24	70·68		
Very fast	62·21	0·0299	0·000678

In column A is recorded the number of revolutions per minute of the disc; in column B the time of exposure in minutes needed to effect the same amount of chemical change; in column C the calculated mean life, in seconds; and in column D the quotient of the mean life and the time required to effect the given amount of chemical change when the solution was exposed without interruption to the light. This quotient should be a constant.

In a third determination light which had been filtered through a solution of iodine was used. The light passed through 5·5 cm. of an aqueous solution of iodine and potassium iodide of such a

strength that the concentration of each of the dissolved substances was twice as great as the corresponding concentration in the solution contained in the reaction vessel. The effect of using such filtered light would, of course, be to render the velocity of chemical change much more uniform throughout the solution. The results are recorded below :

A.	B.	C.	D.
21	293·2		
5	327·8		
5	324·7	0·1212	0·000605
Very fast	282·8		

From any of the above results the mean life of the catalyst in the dark at the temperature of the experiment can be calculated, provided that the rate of the chemical change in the dark is known, and similar assumptions are made concerning the mechanism of the change. The time required to effect the specified amount of change in the dark was found by experiment to be 10,430 minutes. Using the constant determined in the last experiment, we have

the mean life of the catalyst in the dark $= 10430 \times 0{\cdot}000605 =$ 6·31 seconds.

Although we are unable without conducting further research to estimate the errors of the methods described for determining the constant, we believe that the accuracy of the determination is sufficient for present needs, namely, for the purpose of testing a hypothesis.

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JESUS COLLEGE, OXFORD. [*Received, October 30th*, 1925.]

LXXVIII.—*The Action of Alkaline Arsenites on Some Halogenated Organic Compounds.*

By ISIDORE ELKANAH BALABAN.

IT is well known that sulphonic acids, both aliphatic and aromatic, may be obtained by the action of alkali sulphites on some halogenated organic compounds. In view of the chemotherapeutic importance of arsinic acids, it was thought worth while to investigate the action of alkali arsenites on a series of halogenated organic compounds of varying degrees of reactivity, in order, if possible, to delimit the applicability of the method. Meyer (*Ber.*, 1883, **16**, 1440) first employed the method to prepare methyl- and ethylarsinic acids, and it was extended to *n*-propyl-, *iso*amyl-, and benzylarsinic acids by Dehn and McGrath (*J. Amer. Chem. Soc.*, 1906, **28**, 351). Quick and Adams (*ibid.*, 1922, **44**, 809) applied it successfully

to butyl bromide and allyl bromide, whilst Palmer (*ibid.*, 1923, **45**, 3023) applied it to chloroacetic acid. In the aromatic series, Rosenmund (*Ber.*, 1921, **54**, 438) obtained *o*-benzarsinic acid by the action of potassium arsenite on *o*-bromobenzoic acid.

Two glyoxaline derivatives have now been examined containing highly reactive halogen atoms, 4(5)-methyl-5(4)-chloromethylglyoxaline (I) and 5-chloro-1-methyl-2-chloromethylglyoxaline (II), but only the corresponding alcohols could be isolated in poor yield.

(I.) $CH_2Cl\cdot C\cdot NH\rangle CH$ / $CH_3\cdot C{=}N$ (II.) $ClC\cdot NMe\rangle C\cdot CH_2Cl$ / $HC{=}N$

A less reactive glyoxaline compound, 5-chloro-4-nitro-1-methylglyoxaline (III), which had previously been shown to give a sulphonic acid (Balaban and Pyman, J., 1924, **125**, 1564), when heated with potassium arsenite in absolute alcohol gave *4-nitro-5-hydroxy-1-methylglyoxaline* (IV), a very unstable nitroamide resembling in general properties the nitroacetone and nitroacetophenone of Lucas (*Ber.*, 1899, **32**, 600) and Henry (*ibid.*, 1899, **32**, 865).

$ClC\cdot NMe\rangle CH$ / $NO_2\cdot C{=}N$ (III.) $\longrightarrow$ $HO\cdot C\cdot NMe\rangle CH$ / $NO_2\cdot C{=}N$ (IV.) $\longrightarrow$ $OC\cdot NMe\rangle CH$ / $NO_2K{:}C{=}N$

The nitroamide is, however, stable as its *potassium* and *sodium* salts. 2 : 4-Dinitrobromobenzene, which resembles the foregoing in containing a halogen atom activated by a nitro-group, yielded 2 : 4-dinitrophenol, whereas by the action of sodium sulphite in aqueous alcoholic solution it is known to yield 1 : 3-dinitrobenzene-4-sulphonic acid (D.R.-P. 65240). When 8-chlorocaffeine is heated with potassium arsenite in alcohol at 140—180°, a mixture of 8-hydroxy- and 8-ethoxy-caffeine is obtained. Under somewhat parallel conditions (D.R.-P. 74045), 8-chlorocaffeine is known to yield a sulphonic acid when treated with aqueous sodium sulphite. In the foregoing cases where reaction had taken place, the halogen atom was replaced by hydroxyl or ethoxyl. An unexpected result was, however, obtained on examining the action of alkali arsenite on phthalbromomethylimide in acetone solution, as ethylenediphthalimide was isolated.

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot CH_2Br \longrightarrow C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot CH_2\cdot CH_2\cdot N\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4.$$

When it was boiled with 20% aqueous sodium sulphite, *phthalimidomethanesulphonic acid* was obtained in a yield of 13·2% of the theoretical, the main product being phthalic acid (yield 62%), together with a small amount of phthalimide. An attempt to hydrolyse the sulphonic acid to the unknown aminomethanesulphonic

acid proved unsuccessful. Delépine and Demars also failed to obtain this compound by the action of ammonia on chloromethanesulphonic acid (*Bull. Soc. Pharmacol.*, 1922, **29**, 14).

In none of the above cases, although special search was made, was any organic arsinic acid found. If this result be contrasted with the much more general formation of sulphonic acids by the action of alkali sulphite, one is compelled to attribute it to the difference in alkalinity of sulphite and arsenite.

Experimental.

The action of alkali arsenites was examined on the following halogenated organic compounds: 4(5)-*Methyl*-5(4)-*chloromethylglyoxaline* (I). To a mechanically stirred solution of potassium arsenite (24 g.; 10 mols.) in water (30 c.c.) below 0°, 4(5)-methyl-5(4)-chloromethylglyoxaline hydrochloride (2 g.) in absolute alcohol (50 c.c.) was run in during ½ hour. After removal of much arsenic trioxide the mother-liquor was evaporated to dryness in a vacuum, the residue extracted with absolute alcohol, and the extract added to aqueous picric acid; 4(5)-methyl-5(4)-hydroxymethylglyoxaline picrate (1·1 g.; yield, 27·5%) was the sole product obtained. It melted at 180°, alone or mixed with an authentic specimen.

The experiment was repeated in absolute alcohol, but no definite organic products could be isolated.

5-*Chloro*-1-*methyl*-2-*chloromethylglyoxaline* (II), treated as in the above two experiments, yielded 5-chloro-1-methyl-2-hydroxymethylglyoxaline picrate (3 g.; yield, 64%), m. p. 148—149°, and 0·8 g., m. p. 148°, respectively, but no trace of other organic material.

5-*Chloro*-4-*nitro*-1-*methylglyoxaline* (III). The nitro-compound (2 g.) was boiled under reflux with potassium arsenite (5 g.) in absolute alcohol (50 c.c.) for 8 hours, together with a crystal of potassium iodide. On keeping, clusters of yellow needles crystallised (4·2 g.). This product was extracted with water (20 c.c.), and after removal of arsenic trioxide the filtrate was acidified (Congo-paper); 1·07 g. of solid crystallising in fine, colourless needles and decomposing at 106° were then obtained.

4-*Nitro*-5-*hydroxy*-1-*methylglyoxaline* (IV) is soluble in water, alcohol, dilute acids and alkalis, and the usual organic solvents. It cannot be recrystallised, as the solution rapidly becomes dark red, and acquires a strong odour of oxides of nitrogen. It was unsuitable for combustion, as it decomposed very rapidly. In alcoholic solution, the nitroamide gives with ferric chloride an intense brown coloration. It also gives the Liebermann nitroso-reaction. The *potassium* salt, prepared by carefully neutralising the nitro-amide

with dilute potassium hydroxide and evaporating the solution to dryness over sulphuric acid, crystallised in fine, long, yellow needles, decomp. 292°, containing $\frac{1}{2}H_2O$, which was very gradually lost at 95° (Found in air-dried substance: H_2O, 4·7; K, 20·4, 20·6. $C_4H_4O_3N_3K,\frac{1}{2}H_2O$ requires H_2O, 4·7; K, 20·5%). The *sodium* salt, obtained in a similar manner, crystallised in minute, yellow, anhydrous prisms, decomp. 320° (Found: Na, 13·6. $C_4H_4O_3N_3Na$ requires Na, 13·9%).

2 : 4-*Dinitrobromobenzene.* The nitro-compound (2·5 g.), potassium arsenite (8 g.), and absolute alcohol (50 c.c.) were heated under reflux on the water-bath for 8 hours. The product having been worked up as in the previous experiments, 2 : 4-dinitrophenol (1 g.), m. p. 113—114°, alone or mixed with an authentic specimen, was isolated. A further crop (0·5 g.), m. p. 110°, was also obtained.

8-*Chlorocaffeine.* Potassium arsenite (5 g.), 8-chlorocaffeine (2·3 g.), and absolute alcohol (50 c.c.) were similarly heated for 7 hours. The alcoholic mother-liquor gave 0·75 g., m. p. 160°, which after recrystallisation proved to be unchanged material; no products were isolated. The experiment was repeated in aqueous solution, ammonia or methylamine being evolved. After keeping, 0·85 g. of a substance, m. p. 186° alone or mixed with 8-chlorocaffeine, was collected, no other organic matter being obtained. A third experiment was carried out with absolute alcohol in a sealed tube at 140—180° for 8 hours. The alcohol-insoluble portion (0·4 g.) was hydroxycaffeine (m. p. *ca.* 335°), and later crops (0·55 g.), which did not melt at 340°, were hydroxycaffeine contaminated with arsenic trioxide. The residual alcohol-soluble extract (0·45 g.), m. p. 140—142°, was identical with a prepared specimen of 8-ethoxycaffeine, the melting point of the mixture not being depressed.

8-*Hydroxycaffeine,* m. p. 335°, was readily prepared by heating 8-ethoxycaffeine with 16% hydrochloric acid for 10 minutes in the boiling-water bath. It was not obtainable directly from 8-chlorocaffeine by Fischer's process (*Ber.*, 1885, **28**, 2486).

8-*Ethoxycaffeine* was prepared by heating 8-chlorocaffeine (1·5 g.) with potassium hydroxide (1 g.) and absolute alcohol (15 c.c.) under reflux on the water-bath for 6 hours. After removal of the solvent and extraction with water, 8-ethoxycaffeine (0·93 g.; yield, 62%), m. p. 140—142°, was collected; it crystallised in dense, colourless, waxy prisms.

Phthalbromomethylimide. When phthalbromomethylimide (2·4 g.) was heated with potassium arsenite (5 g.) in absolute alcohol (50 c.c.) under reflux for 7 hours, 0·9 g., m. p. *ca.* 210° (alone or mixed with phthalic acid), was collected, no other products being obtained. The experiment was repeated in acetone solution (50 c.c.) from

which 0·95 g. of product, m. p. 230°, was collected. This crystallised in colourless, rectangular prisms from glacial acetic acid, was very sparingly soluble in boiling water, and insoluble in ether (Gabriel, *Ber.*, 1887, **20**, 2225, gives m. p. 232° for ethylenediphthalimide) (Found: N, 8·8 by the Kjeldahl method. $C_{18}H_{12}O_4N_2$ requires N, 8·7%).

Action of Sodium Sulphite on Phthalbromomethylimide.—The bromo-compound (9·1 g.) was boiled under reflux with sodium sulphite (75 c.c. of 20% aqueous solution; 2 mols.) until complete solution was effected ($1\frac{3}{4}$ hours) and kept, when phthalimide (0·35 g., m. p. 232°) was collected. The mother-liquor, on being acidified (Congo-paper), deposited phthalic acid (3·15 g., m. p. 200°), whilst on concentration a further crop (0·85 g., m. p. 200°; total yield 62%) was obtained. From the mother-liquors, by further concentration, phthalimidomethanesulphonic acid was obtained (1·2 g., m. p. 270° with decomp.; yield, 13·2%).

Phthalimidomethanesulphonic acid crystallises from water in long, fine, colourless, rectangular prisms, m. p. *ca.* 295° with decomposition according to the rate of heating; these contain $2{\cdot}5H_2O$. After being dried at 120°, it does not melt even at 320°. It is very soluble in water, but almost insoluble in absolute alcohol (Found in air-dried substance: loss at 120°, 15·8. $C_9H_7O_5NS,2{\cdot}5H_2O$ requires H_2O, 15·7%. Found in substance dried at 120°: N, 5·9 by the Kjeldahl method. $C_9H_7O_5NS$ requires N, 5·8%). The *barium* salt crystallises in long, fine needles which are sparingly soluble in water.

Hydrolysis of the Sulphonic Acid.—The sulphonic acid (0·5 g.) was heated with 20% hydrochloric acid (10 c.c.) for $2\frac{1}{2}$ hours under reflux. On keeping, phthalic acid (0·3 g., m. p. 214°; yield 91%) was obtained, whilst the mother-liquor on concentration gave less than 0·1 g. of ammonium chloride.

The author is greatly indebted to Dr. King for much helpful advice and criticism, and desires to thank Mr. W. Anslow for assistance in this investigation.

THE NATIONAL INSTITUTE FOR MEDICAL RESEARCH,
LONDON, N.W. 3. [*Received, November 21st,* 1925.]

LXXIX.—*The Crystal Structure of Catechol.*

By WILLIAM AUGUSTUS CASPARI.

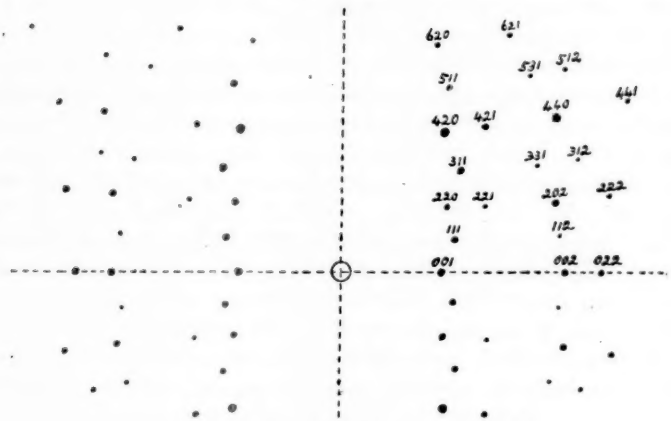
THE crystal morphology of catechol is known from the measurements of Beckenkamp (*Z. Kryst. Min.*, 1900, **33**, 599), who assigned catechol to the monoclinic–prismatic class, axial ratios

1·6086 : 1 : 1·0229, $\beta = 94°15'$. In the present investigation, the rotating-crystal method has been used, and has led to definite data for the crystal cell and the space-group of catechol.

Perfectly developed crystals were obtained without difficulty by the slow evaporation of an aqueous solution. They were in most cases bounded by the three pinacoids; occasionally the prism {110} also appeared; swallow-tail twins about {100} were observed in a few instances.

X-Ray photographs were taken on glass plates through crystals set with the three crystallographic axes as rotation axes. The apparatus was of a simple character with a pinhole beam and requires no description; a Shearer tube with copper anticathode was used.

FIG. 1.



Catechol. Rotation axis a.

Figs. 1, 2, and 3 show the diagrams obtained by projecting the photographs on paper and marking the spots. As a rough guide to intensity, the size of the spots has been proportioned to the intensity of the photographic spots as far as possible. Spots due to $K\beta$ radiation are omitted. The scale of the diagrams corresponds to a distance of 4·8 cm. between the plate and the crystal.

The dimensions of the unit cell follow directly from these photographs. Each spot represents the reflexion from a definite crystal plane, and the spots arrange themselves in layer lines upon which all planes have one index in common; these lines in the case of a flat plate take the form of hyperbolas. The spacing corresponding to the distance of the apex of the first hyperbola from the straight centre line is the length of the unit cell along the axis in question,

and those of further hyperbolas are consecutive multiples. Calculations are based on the formula

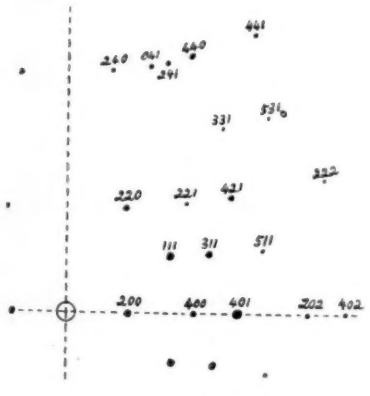
$$a(\text{or } b \text{ or } c) = n \times 1{\cdot}54 \,/\cos\mu \text{ Å.},$$

where n is the series number of the layer line, and 1·54 Å. the wavelength of copper $K\alpha$ radiation. The following cell dimensions were thus obtained:

along a axis, mean of 5 layer lines, $a = 17{\cdot}46$ Å.
,, b ,, ,, 4 ,, ,, $b = 10{\cdot}74$ Å.
,, c ,, ,, 2 ,, ,, $c = 5{\cdot}48$ Å.

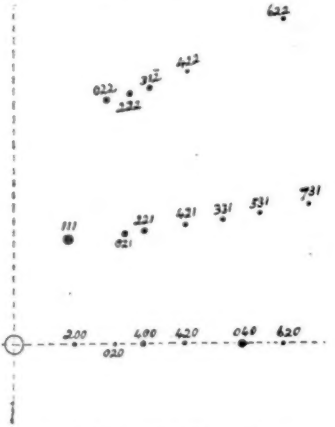
The ratios of these dimensions, *viz.*, 1·62 : 1 : 0·51, agree with the goniometric axial ratios except that c has been stated at double its

FIG. 2.



Catechol. Rotation axis b.

FIG. 3.



Catechol. Rotation axis c.

proper length by Beckenkamp. The axial ratios of catechol should be written 1·6086 : 1 : 0·5114.

To find the number of molecules in the unit cell, we have as the weight of the cell, the density of catechol being 1·375,

$$17{\cdot}46 \times 10{\cdot}74 \times 5{\cdot}48 \times \sin 94°15' \times 1{\cdot}375 = 1403 \times 10^{-24} \text{ g.}$$

The weight of the molecule being $110 \times 1{\cdot}65 \times 10^{-24}$ g., the quotient is 7·8. That is, there are eight molecules in the unit cell. Indices can now be assigned to the various photographic spots by calculating the spacing d of each and applying the stereometric formula proper to the monoclinic system, which in the present case takes the form

$$1/d^2 = 0{\cdot}0033h^2 + 0{\cdot}0087k^2 + 0{\cdot}0331l^2 - 0{\cdot}0016hl.$$

The indices of all the planes observed are tabulated below.

Rotation Axis a.			*Rotation Axis* b.			*Rotation Axis* c.		
Plane.	*d* obs.	*d* calc.	Plane.	*d* obs.	*d* calc.	Plane.	*d* obs.	*d* calc.
{001}	5·44	5·49	{200}	8·81	8·70	{200}	8·67	8·70
{002}	2·71	2·75	{400}	4·42	4·35	{020}	5·39	5·36
{022}	2·41	2·45	{401}	3·46	3·54	{400}	4·34	4·35
{111}	4·73	4·79	{202}	2·67	2·68	{420}	3·32	3·38
{112}	2·69	2·66	{402}	2·36	2·41	{040}	2·67	2·68
{220}	4·58	4·56	{111}	4·73	4·79	{620}	2·49	2·55
{221}	3·58	3·58	{311}	3·76	3·88	{111}	4·75	4·79
{202}	2·62	2·68	{511}	2·86	2·93	{021}	3·80	3·84
{222}	2·34	2·39	{220}	4·52	4·56	{221}	3·63	3·58
{311}	3·76	3·88	{221}	3·55	3·58	{421}	2·92	2·96
{331}	2·68	2·70	{421}	2·96	2·96	{331}	2·56	2·70
{312}	2·44	2·50	{222}	2·31	2·39	{531}	2·33	2·31
{420}	3·38	3·38	{331}	2·64	2·70	{731}	2·05	2·07
{421}	2·94	2·96	{531}	2·33	2·31	{022}	2·44	2·45
{440}	2·30	2·28	{240}	2·53	2·56	{222}	2·32	2·39
{441}	2·12	2·14	{041}	2·42	2·41	{312}	2·27	2·34
{511}	2·88	2·93	{241}	2·33	2·34	{422}	2·15	2·20
{531}	2·35	2·31	{440}	2·28	2·28	{622}	1·91	1·94
{512}	2·12	2·19	{441}	2·11	2·14			
{620}	2·55	2·55						
{621}	2·27	2·38						

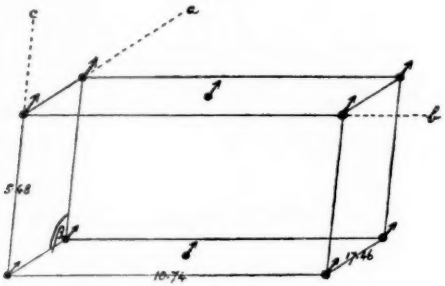


FIG. 4.

The table shows that in all cases the sum of the indices h and k is an even number, and that there are no other regularities connecting the various indices. From this it follows that if the cell be represented by four equal molecules at the corners of a parallelipiped, there must be molecules of the same orientation in the centres of the {001} faces (Fig. 4). Hence the space-lattice is Γ_m' and, further, the space-group is narrowed down to C_{2h}^3. For this space-group, eight asymmetric molecules is the full number permissible; the catechol molecule, therefore, is without any intrinsic symmetry in the crystalline state. Each primary molecule, as shown in Fig. 4, must have three other differently oriented molecules near it.

As regards the actual disposition of the molecules in the crystal, we have as arguments the above symmetry data, the crystal

habit, and the size and shape of the catechol molecule. The evidence at hand points to a simple parallelipipedic arrangement, such that all the molecules are as it were skewered along the *b* axis, with the plane of the benzene rings lying parallel to *a* and *c* and the hydroxyl groups pointing pairwise alternately backward and forward along the *a* axis. Detailed discussion may, however, be deferred pending the examination of 2 : 3-dihydroxynaphthalene and 2 : 3-dihydroxyanthracene, which is now in progress. The above arrangement is in harmony with the reticular densities of the crystal faces; these would work out as follows :

{100} face,	1 molecule in	14·7	Å^2.
{001} ,,	,,	23·5	,,
{010} ,,	,,	48·0	,,
{110} ,,	,,	57·0	,,

In the majority of the crystals, {100} is decidedly the most developed and {010} the least developed face, whilst {110} occurs only sporadically; the order of the reticular densities is thus the same.

The author desires to express his indebtedness to Sir William Bragg, F.R.S., and to his fellow-workers at the Davy Faraday Laboratory for the helpful interest taken by them in this investigation; also to the authorities of the Royal Institution for apparatus and laboratory facilities.

DAVY FARADAY LABORATORY,
ROYAL INSTITUTION. [*Received, November 25th,* 1925.]

LXXX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part I. The Elimination of Hydrogen Chloride from* 3 : 4′*-Dinitrostilbene Dichloride.*

By HAROLD AINSWORTH HARRISON and HAROLD WOOD.

FLÜRSCHEIM was the first to point out the important principle that the alternate effects produced by substituents in aromatic nuclei can be rendered conspicuous by comparing the properties of isomeric *m*- and *p*-disubstituted derivatives. With groups in these two positions the possibility of ring closure is almost eliminated and anomalies caused by steric hindrance are largely curtailed, whilst the general polar effects are approximately equal. The present research was undertaken with the idea of testing the accuracy of

certain apparently unequivocal forecasts derived by application of the alternate polarity rule to the diphenylethane series. The theory of non-polar alternating affinity, on the contrary, does not appear to afford any trustworthy *a priori* guidance in the types of reaction selected for investigation.

The dichlorides and dibromides of αβ-unsaturated acids, when deprived of one molecule of halogen hydride, invariably lose the β-halogen atom. It seemed desirable, therefore, to ascertain whether similarly unidirectional influences could be discovered in the dihalides of unsymmetrically substituted stilbene derivatives. The effect of two nitro-groups in the 3- and 4′-positions is cumulative and a strong difference in the reactivity of the two halogen atoms should accrue. The removal of one molecule of halogen hydride should therefore result in the preferential formation of one or other of the two possible monochlorostilbenes. Aa a matter of fact, *α-chloro*-4 : 3′-*dinitrostilbene* was the sole product of reaction, and this is in entire agreement with polarity principles.

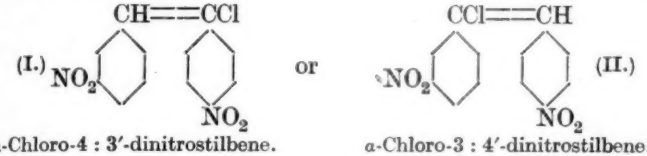
3 : 4′-Dinitrostilbene had previously been prepared by Cullinane (J., 1923, **123**, 2060) by the condensation of *p*-nitrophenylacetic acid and *m*-nitrobenzaldehyde in presence of piperidine at 100° for 1 hour. Exact repetition of his method by the present authors resulted, however, in the isolation of a totally different product. Cullinane's supposed dinitrostilbene consisted of yellow needles, m. p. 155° (yield not stated), which gave green solutions in various organic solvents. The dinitrostilbene obtained by us, having been washed many times with boiling alcohol and recrystallised from glacial acetic acid, melted at 217°, and was sparingly soluble in most solvents, forming only pale yellow solutions.

From the alcoholic washings three other products were isolated in small quantity : *p*-nitrotoluene, formed by the partial decomposition of *p*-nitrophenylacetic acid by piperidine, and the *piperidine* salts of the two stereoisomeric forms of 3 : 4′-dinitro-α-phenylcinnamic acid, resulting from loss of water without carbon dioxide. Both of these acids were subsequently synthesised. They could be decarboxylated to give the same dinitrostilbene by heating with piperidine. Their properties will be described in a future paper.

Preliminary investigation showed that 3 : 4′-*dinitrostilbene dibromide* * on heating with pyridine lost both atoms of bromine; the stilbene was therefore converted into a mixture of *dichlorides*, from each of which (although with much greater facility in the case of the low-melting β-variety), by prolonged heating with pyridine, one

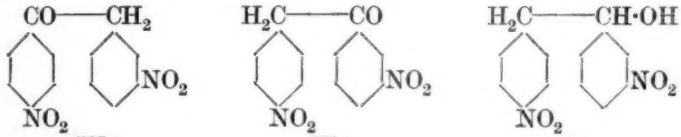
* A detailed description of this dibromide will be given in a subsequent paper.

molecule of hydrogen chloride was eliminated, with the formation of only one monochlorodinitrostilbene, having one of the configurations I and II.



α-Chloro-4 : 3′-dinitrostilbene. α-Chloro-3 : 4′-dinitrostilbene.

The chlorostilbene was eventually * decomposed by warm concentrated sulphuric acid, with the formation of a coloured intermediate compound (not isolated). This on decomposition with water passed through the transitory enol form to produce 4-*nitrophenyl* 3-*nitrobenzyl ketone* (III).



That this ketone had the structure shown was proved by oxidising the intermediate aldol, 3 : 4′-*dinitro*-αβ-*diphenylethyl alcohol*, isolated as a by-product from the stilbene condensation and therefore possessing the configuration (V), with chromic acid in acetic acid solution, when the isomeric 3-*nitrophenyl* 4-*nitrobenzyl ketone* (IV) was obtained.† Another proof of the constitution of (III), by its synthesis from 3 : 4′-dinitro-α-phenylcinnamamide, will be described shortly.

Each of these ketones (III and IV) was converted into the corresponding monochlorodinitrostilbene by treatment with phosphorus pentachloride, and although these two products melted at approximately the same temperature, a mixed melting point determination showed a depression of 20°, and further, each chlorodinitrostilbene, on treatment with sulphuric acid as before, was reconverted into the corresponding ketone.

Without doubt the monochlorodinitrostilbene formed by loss of the elements of hydrogen chloride from 3 : 4′-dinitrostilbene dichloride is I and not II.

* Prolonged boiling with silver acetate in acetic acid, with potassium acetate, or with formic acid was ineffectual. An attempt to prepare the ozonide met with no greater success.

† Finzi had shown (*Monatsh.*, 1905, **26**, 1128) that oxidation of a substituted deoxybenzoin to the benzil cannot be carried out with chromic acid in acetic acid.

EXPERIMENTAL.

3 : 4′-*Dinitrostilbene.*—A mixture of *p*-nitrophenylacetic acid (76 g.) and *m*-nitrobenzaldehyde (63·5 g.) was heated with piperidine (13 g.) at 110° for 1 hour (carbon dioxide and water were expelled; the liquid then set to a semi-solid mass); thereafter the temperature was raised to 150° * during 2 hours. The product was boiled with alcohol (200 c.c.) until the solid cake had disintegrated, and the dinitrostilbene was then filtered off, pulverised, and repeatedly washed with boiling alcohol (about 300 c.c.) until it was bright yellow. It crystallised from acetic acid, nitrobenzene or pyridine in yellow needles, m. p. 217° (Found : C, 62·35; H, 3·75. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7%). It is slightly soluble in hot benzene, acetone, ethyl acetate, or chloroform, but very sparingly soluble in boiling alcohol. The yield was 30%. On standing, the mother-liquor and washings deposited a dark brown, viscous oil which could not be purified; treatment of this with cold strong sulphuric acid increased the total yield of dinitrostilbene to 55%.

3 : 4′-*Dinitro-αβ-diphenylethyl Alcohol* (V).—After removal of this oil, addition of water precipitated a light yellow solid which, after crystallisation from acetic acid and then from alcohol, melted at 147—148° (Found : C, 58·1; H, 4·3. $C_{14}H_{12}O_5N_2$ requires C, 58·3; H, 4·2%). This substance is soluble in alcohol, acetic acid, ethyl acetate, or acetone, and sparingly soluble in ether or benzene. Heating with piperidine or treatment with cold strong sulphuric acid produces the dinitrostilbene. Slow evaporation of the solution after removal of the aldol compound caused the separation of a little *p*-nitrotoluene, and on long standing the residual liquors deposited thin leaflets which crystallised from alcohol in straw-coloured needles, m. p. 168—169° (Found : C, 59·7; H, 5·2. $C_{20}H_{21}O_6N_3$ requires C, 60·15; H, 5·3%). This compound is therefore the *piperidine* salt of one of the two stereoisomeric 3 : 4′-dinitro-α-phenylcinnamic acids, m. p. 221°.† If the temperature of condensation is allowed to rise to 160° after 1 hour, the yield of dinitrostilbene is even less than usual, much more *p*-nitrotoluene being formed. After removal of the normal reaction products (no pure aldol can be isolated) a crop of crystals separates, which after crystallisation from alcohol consists of bright yellow needles, m. p. 204—205° (decomp.) (Found : C, 59·85; H, 5·5. $C_{20}H_{21}O_6N_3$ requires C, 60·15; H, 5·3%). This is the *piperidine* salt of the other stereoisomeric substituted cinnamic acid, m. p. 205·5°.†

* Above this temperature much decomposition takes place.

† The free acids were obtained by treatment of the piperidine salts with warm sodium carbonate solution, and subsequent acidification; the melting points were not depressed by admixture with authentic samples.

α- *and* β-*Forms of* 3 : 4′-*Dinitrostilbene Dichloride.*—Finely divided 3 : 4′-dinitrostilbene (20 g.) was suspended in chloroform (750 c.c.),* and dry chlorine passed in during 4 hours. After standing for 4 days, the excess of chlorine was removed from the filtered solution by shaking carefully with dilute sodium bisulphite, and then with sodium hydroxide. After having been washed and dried, the chloroform solution was evaporated to a small bulk until deposition of the dichloride commenced (concentration beyond this stage tends to blacken the product). When cold, the white crystals were filtered off, washed with a little chloroform, and dried (15 g.; 60% yield). They consisted of a mixture of the α- and β-forms, and melted at 188—196°. By two crystallisations from acetic acid the pure α-form could be obtained in thin plates, m. p. 207° (Found: Cl, 20·9. $C_{14}H_{10}O_4N_2Cl_2$ requires Cl, 20·8%). The more soluble β-form, m. p. 132—138°, was never obtained quite pure (Found: Cl, 21·1%). Both forms are appreciably soluble in alcohol.

α-*Chloro*-4 : 3′-*dinitrostilbene* (I).—Preliminary investigation having shown that the α- modification of the dichloride is much more stable to pyridine than the β-, the crude mixture of dichlorides (75 g.) was heated (water-bath) with pyridine (160 g.) for 90 hours. On cooling, bright yellow, glistening needles of the monochlorodinitrostilbene crystallised out, which after recrystallisation from acetic acid melted at 161° (Found: C, 54·9; H, 3·1; Cl, 11·5. $C_{14}H_9O_4N_2Cl$ requires C, 55·2; H, 2·95; Cl, 11·6%). Precipitation of the mother-liquors with alcohol resulted in a further small quantity (total yield = 77%). No other product was isolated.† This compound crystallises well from pyridine, acetic or formic acid, benzene, chloroform, or acetone. It is but sparingly soluble in alcohol, ether, or carbon tetrachloride.

4-*Nitrophenyl* 3-*Nitrobenzyl Ketone* (III).—Finely powdered α-chloro-4 : 3′-dinitrostilbene (I) (5 g.) was gently warmed with strong sulphuric acid (20 c.c.) during 1 hour (above 60°, charring takes place). When the evolution of hydrogen chloride had ceased, the deep red solution was cooled and poured on to ice. The almost white precipitate was crystallised from alcohol, and then from acetic acid; clusters of white needles, m. p. 134°, were thus obtained

* A smaller quantity of solvent is inadvisable, owing to the slow speed of absorption of chlorine by the stilbene.

† The liquors were concentrated almost to dryness on the water-bath and warmed with strong sulphuric acid. After the vigorous evolution of hydrogen chloride (chiefly from the pyridine hydrochloride) had ceased, the product was poured into water, and the lutarious deposit crystallised from alcohol (charcoal). It melted at 129° and did not depress the melting point of III. It had therefore been formed from the same chlorodinitrostilbene.

(Found : C, 58·5; H, 3·6. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·5%). This ketone is easily soluble in all the usual solvents except ether, light petroleum, or carbon tetrachloride. It gives a *semicarbazone* which crystallises from alcohol in pale yellow needles, m. p. 219°. Treatment of the ketone at its melting point with phosphorus pentachloride reconverted it into the monochlorodinitrostilbene.

3-*Nitrophenyl* 4-*Nitrobenzyl Ketone* (IV).—A solution of the aldol compound (V) (4·5 g.) in hot glacial acetic acid (45 c.c.) was cooled to 50° without allowing deposition of solid, treated with a 10% solution of chromic acid [prepared from crystalline sodium dichromate (7·5 g.), sulphuric acid (10 g.), and water (35 g.)] during 1 hour, and then, while still warm, with water (10 c.c.). The ketone which separated crystallised from 95% alcohol in pearly plates (yield 75%), m. p. 102° (Found : C, 58·65; H, 3·45. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·5%). The solubilities of this ketone approximate very closely to those of the isomeric ketone (III), m. p. 134°. It gives a *semicarbazone* which crystallises from alcohol in bright yellow rhombs, m. p. 230°.

α-*Chloro*-3 : 4′-*Dinitrostilbene* (II).—Treatment of the ketone (IV) at its melting point (brine-bath) with phosphorus pentachloride furnished the corresponding monochlorodinitrostilbene in fair yield; on crystallisation from acetic acid, it formed small clumps of light brown needles, m. p. 162° (Found : C, 55·0; H, 3·0; Cl, 11·8. $C_{14}H_9O_4N_2Cl$ requires C, 55·2; H, 2·95; Cl, 11·6%). A mixture of the two isomeric monochlorostilbenes melted at 142—145°. The solubilities of this isomeride (m. p. 162°) are almost identical with those of the other (m. p. 161°). The degrees of stability, too, are comparable, since prolonged boiling with formic acid or with silver acetate in acetic acid does not remove the chlorine atom. Pyridine is also without action. Concentrated sulphuric acid at 60° converts it into the ketone (IV) from which it was derived, but so far as could be ascertained there was no difference in the rate of decomposition of the two monochlorodinitrostilbenes.

Action of Concentrated Sulphuric Acid.—The dinitrostilbene furnishes a bright red solution, from which the unchanged product is recovered on dilution with water : both monochlorodinitrostilbenes (I and II) give deep red solutions on warming and evolve hydrogen chloride vigorously; they char considerably at 80° : the dinitrostilbene dichloride yields a faintly pink solution, with very slight evolution of gas; it chars somewhat at about 80° : the dinitrostilbene dibromide gives a pink colour and evolves hydrogen bromide at 70—80°; there is no sign of charring, and the product after dilution with water and crystallisation from alcohol still contains bromine.

One of us (H. W.) desires to express his gratitude to the Department of Scientific and Industrial Research for a maintenance grant, and the other (H. A. H.) to the Chemical Society Research Fund for a grant which has defrayed the cost of materials. We are also indebted to Professor Lapworth for suggesting the line of research.

THE UNIVERSITY, MANCHESTER. [*Received, November 27th*, 1925.]

LXXXI.—*The Budde Effect in Bromine. Part I. The Photoactive Constituent of Wet Bromine.*

By BERNARD LEWIS and ERIC KEIGHTLEY RIDEAL.

THE experiments of Dixon and of Baker (*Rep. Brit. Assoc.*, 1894, p. 493; J., 1884, **45**, 611) on the influence of small traces of water on physical and chemical changes have led to the theory of internal equilibrium of Smits ("The Theory of Allotropy," Longmans and Co.) in which it is assumed that water acts as a catalyst in accelerating the attainment of equilibrium between various polymeric or allotropic forms of simple molecules in homogeneous systems which were originally in metastable states. To exert this catalytic activity it must be assumed that the water makes a temporary complex with the reactant, which complex must be capable of excitation or activation more readily than the reactant molecules themselves.

The earlier experiments of Budde (*Pogg. Ann.*, 1871, **144**, 213; *Wied. Ann.*, 1879, **6**, 477), Mellor (J., 1902, **81**, 1280), and Bevan (*Phil. Trans.*, 1903, **202**, *A*, 71) as well as those of Pringsheim (*Wied, Ann.*, 1887, **32**, 385), Richardson (*Rep. Brit. Assoc.*, 1888, p. 89). Shenstone (J., 1897, **71**, 471), and Cordier (*Monatsh.*, 1900, **21**, 660) revealed the fact that dry chlorine differed from moist chlorine in that on exposure to radiation, especially in the blue and violet portion of the spectrum, moist chlorine underwent expansion, but dry chlorine, although absorbing the radiation, showed no such expansion. This "Budde" effect has likewise been noted by Budde (*loc. cit.*) and by Ludlam (*Proc. Roy. Soc. Edinburgh*, 1924, **44**, 197) in the case of bromine.

The early experiments made it clear that the expansion in the moist halogen was due to the conversion of absorbed radiation into thermal energy of molecular agitation and it was assumed from this fact that, since the Budde effect is still obtainable in a region of the spectrum in which the quantum is small (in the case of bromine a Budde expansion is still noticeable at $\lambda = 5800$ Å., whilst according to Franck [Photochemical meeting, Oxford, 1925], from a consideration of the distribution of the absorbed energy between

rotational, oscillatory, and electronic quantum states of the molecule, dissociation of the molecule cannot be effected with a wavelength greater than $\lambda = 5000$ Å.), the thermal effects are not produced by a primary activation of a bromine molecule followed by a splitting into atoms with their subsequent recombination. It has also been shown by Sir J. J. Thomson (*Proc. Camb. Phil. Soc.*, 1901, **11**, 90) that the formation of charged ions according to the reaction $Br_2 \rightleftarrows Br^{\cdot} + Br'$ does not occur, a view which can likewise be demonstrated to be improbable from a comparison of the magnitudes of the energies required for dissociation into atoms and ions respectively. How the moisture caused the conversion of radiant into kinetic energy was not elucidated. We may note, however, that Bevan (*loc. cit.*) postulated the existence of complexes such as $(Cl_2)_x(H_2O)_y(H_2)_z$ in the water-sensitised hydrogen–chlorine mixture, and on analogy with this conception it might be argued that a hydrate $(Br_2)_x(H_2O)_y$ was the photoactive constituent responsible for the Budde effect. Alternatively it might be suggested that in the metastable, freshly distilled, dry halogen a photosensitive polymeride of bromine is absent, but is present when the inner equilibrium is attained with the aid of the catalytic water. With the exception of the work of Coehn and Jung (*Z. physikal. Chem.*, 1924, **110**, 705) on the hydrogen–chlorine reaction, no quantitative work on the influence of water on such reactions has been accomplished and it appeared of interest to examine the Budde effect in bromine in more detail.

It may be stated at the outset that the experimental data support the hypothesis that the Budde effect is due to a photosensitive bromine hydrate of composition Br_2,H_2O and that the water does not function as a catalyst in the formation of a photosensitive polymeride of bromine. Having established this point, it was necessary to investigate the properties of this hydrate in more detail such as its heat of formation, the value of the equilibrium constant of the reaction $Br_2 + H_2O \rightleftarrows H_2O,Br_2$ and the distribution of the hydrate, *i.e.*, the partition of the hydrate between the surface and bulk phases in the reaction vessel.

Finally, it was decided to investigate how far the absorption spectrum of the hydrate differed from that of bromine vapour, to evaluate its absorption coefficient, and to suggest a hypothesis as to the mechanism of operation of the Budde effect.

The importance of these points would appear not to be confined to the Budde effect alone, for if hydrates do exist in the gas or liquid phases of non-polar, or feebly polar substances, it is to be anticipated that the walls of the containing vessel which adsorb water readily will likewise adsorb the hydrate. Thus the partition

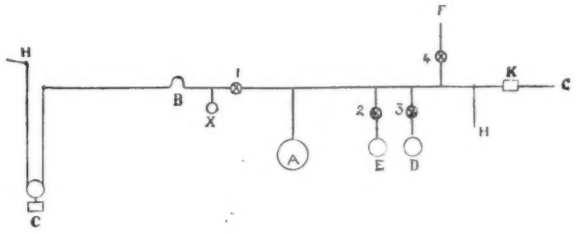
of the hydrate between the bulk and surface phases will obey an equation of the type found to hold in the isothermal adsorption of vapours and will prove an important factor in the relative rates at which reactions, which are *ex hypothesi* due to this hydrate, occur in the two phases.

Again, whilst dry bromine does absorb light within a large portion of the spectral region which causes the Budde effect in wet bromine, no thermal effects are to be noted. It follows that the apparent absorption is fictitious, for the light must be re-emitted as fluorescent light or scattered from the molecules. The hydrate molecules, on the other hand, absorb the light which is subsequently converted into thermal energy. The data from absorption spectra clearly do not distinguish between these two phenomena. The influence of water in cutting down the fluorescence of dry hydrogen and oxygen exposed to illumination of a quartz mercury vapour light recently noted by Baker* (J., 1925, **127**, 1990) and the fluorescence of dry active hydrogen yielding the line $\lambda = 3064$ Å., a water vapour line (Bonhoeffer, *Z. physikal. Chem.*, 1925, **116**, 39), would appear to be a phenomenon similar to that occurring in bromine.

Experimental.

Two forms of apparatus were employed for determination of the effect of alteration in the partial pressures of the bromine and

Fig. 1.



water on the magnitude of the Budde effect. For low partial pressures of water, the following method was devised. The reaction vessel, *A*, of 20 c.c. capacity, consisted of a bulb with plane-parallel sides, 2·35 cm. apart, connected on one side by capillary glass tubing to the phosphoric oxide tube, *X*, and the glass gauge, *B*. On the other side capillary connexions were made to the bromine and water reservoirs *D* and *E*, the drying train, *F*, the McLeod gauge, *H*, and mercury vapour pump line, *G*.

During evacuation of the reaction vessel the gauges and reactant

* Communicated at a meeting of the Society.

reservoirs were temporarily disconnected by capillary glass inner seals 1, 2, 3, 4, which were provided with iron rods enclosed in glass permitting of fracture of the seals with the aid of an electromagnet. Between the diffusion pumps, *G*, and the apparatus a liquid air-trap was placed to prevent back-diffusion of mercury vapour. The gauge, *B*, consisted of a well-annealed (5 months), collapsed elliptical glass bulb forming a Bourdon indicator, attached to a 30 cm. glass pointer, to the end of which one arm of a quartz bifilar suspension for a mirror, *C*, was attached. The mirror was steadied by means of a mica vane dipping in water, the surface tension of which was lowered by the addition of a drop of oleic acid, thus permitting unhindered movement of the mirror. A spot of light from the mirror on a scale one metre away was followed. The sensitivity of the gauge could be varied by alteration, with the aid of a micrometer screw, of the position of the left arm, *H*, of the bifilar suspension; pressure changes of 1/120 mm. of mercury could be registered when it was in most sensitive adjustment. The gauge was calibrated with the aid of a mercury manometer and eye-piece, frequent calibration showing but little change in the characteristics.

The apparatus employed for the higher vapour pressures of water was similar to that described above, but in place of internal seals, stopcocks, lubricated by two rims of chlorinated odourless wax, were employed. In place of the water reservoir, a bulb containing sodium sulphate decahydrate was employed as source of water vapour, which was connected to the reaction vessel and pump through a small dosing apparatus of 0·3 c.c. capacity permitting of admission of small quantities of water vapour to the dry bromine. The source of light was a 1000 c.p. point light, parallel rays being obtained with a collimator, the reaction vessel being mounted in a plane-sided trough through which water was circulated from a thermostat. Between the collimator and the trough was placed a smaller trough in which the requisite colour filters could be placed.

Materials.—The bromine was prepared by distillation of the purest obtainable bromine, twice over zinc oxide and once over freshly prepared phosphoric oxide in a closed system which had originally been baked out. The bromine was stored over phosphoric oxide in a sealed vessel and was not used for the dry experiments until 9 months later. The data of Ramsay and Young (J., 1886, **49**, 453) were employed for the vapour pressure at various temperatures.

The sodium sulphate decahydrate was prepared by triple crystallisation and partial desiccation. The dissociation vapour pressure

at 0° employed was 2·77 mm., from the value given by Baxter and Lansing in the Landolt–Bornstein tables.

The water employed was pure conductivity water, and the vapour pressures were calculated with the aid of the equation of Nernst (*Verh. deut. physikal. Ges.*, 1907, **11**, 313): $\log_{10} P_{\text{mm.}} = -\frac{2611}{T} + 1{\cdot}75 \log T - 0{\cdot}00210T + 6{\cdot}5343$, substantiated experimentally to 100° K. by S. Weber (*Communication Lab. Leyden*, 1915, **14**, 150A).

Three different vapour pressures were employed at temperatures corresponding to the freezing points of toluene, ethyl acetate and chloroform. The values are in the following table:

Substance.	Temperature.	V. p. above the ice in mm. Hg.
Melting toluene	−93°	$3{\cdot}9 \times 10^{-5}$
„ ethyl acetate	−83	$2{\cdot}3 \times 10^{-4}$
„ chloroform	−63	$5{\cdot}3 \times 10^{-3}$

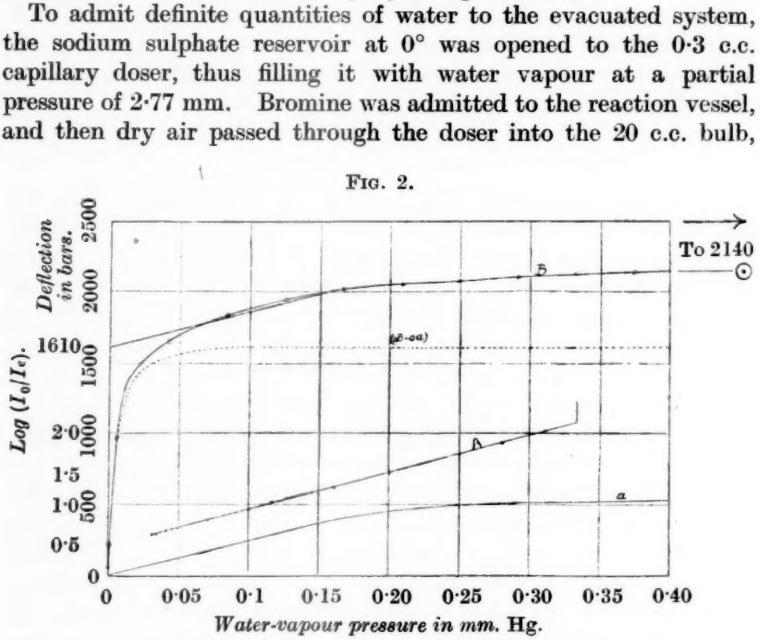
Method of Operation.—The method of operation employed was as follows. The reaction vessel was placed in an electric furnace and the capillaries and connexions up to the seals were wound with nichrome wire and thoroughly lagged with asbestos. One or two small parts were heated frequently with a Bunsen flame. A vacuum (less than 10^{-6} mm. Hg) was maintained in the system at 400° for 5 days. The seal connecting the system to the ice maintained in liquid air was first broken with the connexion still open to the pumps. The high vacuum was rapidly reached again, the pumps were disconnected, the liquid air was replaced by melting toluene, and the water vapour allowed to pass into the reaction bulb. When equilibrium was attained (over an hour), the capillary tube leading to the water-vapour container was sealed under the blow-pipe, and the reservoir removed. Dry bromine at the required partial pressure (the bromine reservoir had been previously evacuated and maintained at a desired temperature) was admitted, and the bromine reservoir removed in a similar manner. Finally, dry air was admitted to atmospheric pressure, and the connexion sealed. The phosphoric oxide tube, *X*, was sealed and the connexion to the gauge established by breaking the capillary seal (1). Finally, the tube containing the iron rod at seal (1) was sealed and removed.

The reaction vessel was brought to a uniform temperature by the circulating water, and the deflection on the gauge observed for various distances of the lamp and with various colour filters (Wratten light filters). Finally, the gauge setting was calibrated. Four separate experiments were carried out in this manner, one with dry bromine–air mixture, in which no Budde effect was noted under the most intense illumination, and three with water vapour at the partial pressures given above.

For determination of the Budde effect at higher water-vapour pressures, taps instead of internal seals were employed and evacuation was effected with a Toepler pump instead of the diffusion pumps. On admission of dry bromine and air to the reaction vessel a small Budde effect was always noticeable under strong illumination, indicating that traces of water vapour (0·001 mm.) could not be eliminated entirely by this procedure.

To admit definite quantities of water to the evacuated system, the sodium sulphate reservoir at 0° was opened to the 0·3 c.c. capillary doser, thus filling it with water vapour at a partial pressure of 2·77 mm. Bromine was admitted to the reaction vessel, and then dry air passed through the doser into the 20 c.c. bulb,

FIG. 2.



thus sweeping the water vapour into the reaction system. Any number of doses could be admitted in this manner.

Neither with air nor with dry bromine on illumination was the slightest change in pressure observed, but in the presence of moisture a rapid rise in pressure, approaching an equilibrium value within 20 to 30 seconds, was always obtained. On cutting off the illumination, the light spot of the gauge indicator returned to its initial position.

An investigation of the magnitude of the Budde effect with various light filters showed (the Wratten filters 15, 16, 21, 25 as well as various combinations were permeable to photochemically active light) that light of wave-length longer than $\lambda = 5800$ Å. produced no detectable effect; light within a region 5600 Å. to 5500 Å. was particularly effective. Accordingly, a filter combination transmitting red light and light from 5400 Å. to 5700 Å.

with a maximum permeability near 5500 Å. was employed for all quantitative experiments.

An investigation revealed that the energy distribution in the various wave-lengths between 5000 Å. and 6000 Å. of the point light as measured with a thermopile and galvanometer was uniform, thus a mean of the effective extremes of the light filter could be assumed.

Results.—In the curve (Fig. 2) is given the relationship between the Budde effect in bars (dynes per sq. cm.) as a function of the partial pressure of the water vapour at a constant bromine pressure of 158 mm. and a temperature of 40°. Some of the values obtained, from which the curve was plotted on a very large scale so as to permit of accurate analysis, are in the following table:

Partial press. of Br, 158 mm. Temp. of bath, 40°. Distance of lamp, 15 cm.

Press. of H_2O in mm. Hg.	Deflection in bars.	Press. of H_2O in mm. Hg.	Deflection in bars.
0	0	$8{\cdot}3 \times 10^{-2}$	1830
$3{\cdot}9 \times 10^{-5}$	66	$1{\cdot}245 \times 10^{-1}$	1950
$2{\cdot}3 \times 10^{-4}$	226	$1{\cdot}66 \times 10^{-1}$	2020
$5{\cdot}0 \times 10^{-3}$	958·8	$3{\cdot}32 \times 10^{-1}$	2140
$4{\cdot}15 \times 10^{-2}$	1640	$5{\cdot}395 \times 10^{-1}$	2140

It will be noted that the curve may be divided into three portions; for low partial pressures of water up to 0·005 mm. the Budde effect rises rapidly; this is followed by an almost linear portion of the curve (0·03 mm. to 0·16 mm.) in which the Budde effect increases proportionally to the increase in the water-vapour pressure; finally, at high water concentrations, the Budde effect increases less rapidly, attaining a maximum of *ca.* 2140 bars at a partial pressure of 0·3320 mm., which is not affected even when the water-vapour pressure is increased to 0·5810 mm. It was suspected that this apparent maximum as well as that shown in Fig. 3 was due to complete absorption of the active radiation. Proof of the correctness of this view was obtained in the following ways. The Budde effect for these high water concentrations was found to be dependent on the distance of the source of illumination from the bulb as shown by the following data, *a* being the distance (cm.) of the lamp from the reaction vessel, and *b* the deflection in scale-divisions:

a	72	62	52	42	32	22	15·5	11
b	5	7	10	16	25·5	44—45	82	160

It might indeed be argued that the flattening of the curve is caused by increased heat radiation outward, as the Budde effect increases. In the following manner this view was found to be incorrect, within the magnitudes of the Budde effect, and our first view more directly confirmed. A very fine platinum filament,

terminating in thick platinum wires, was sealed in the reaction vessel, which was filled with bromine and water vapour to the desired partial pressures. Several partial pressures of bromine were employed. An electric current was passed through the spiral filament and from a knowledge of the current passing and the potential difference across the spiral the heat evolution in calories per second to give various expansions measured on the gauge could readily be determined. Fig. 4 shows the curve, average values of deflections for different bromine concentrations (these varied only a little) being plotted as ordinates against calories per second developed by the spiral as calculated from $H = 0{\cdot}24RI^2$. It will be observed that the curve bends only slightly within the limits employed. If, now, one takes two deflections on curve A (Fig. 3) and plots as abscissa the heat corresponding, as obtained from Fig. 4, and then from this interval one obtains the scale plotting in place of bromine pressure as abscissa, the calories per sec. (Curve C), one observes that the two curves coincide along the rectilinear portion. It is clear that if the falling off of the Budde effect were due to increased heat radiation, the two curves should coincide throughout. But the Budde effect falls off much more rapidly, supporting the view that the maximum is due to complete absorption of the actinic rays.

The following furnishes additional proof for the total extinction of the actinic rays at the maximum. When the surface is practically saturated, the course of the curve is governed by the absorption of light in accordance with Beer's law.

$$I_\epsilon = I_0 e^{-k(dc+K)}$$

where K is the constant concentration of hydrate on the surface (see later, p. 593).

Hence $\log (I_\epsilon/I_0) = -k(dc + K)$ or $\log (I_0/I_\epsilon) = k'c + K'$.

C, the concentration of the hydrate, is proportional to the water concentration in the bulk phase. Curve A (Fig. 2) shows that from 0·03 mm., where the surface concentration is practically up to saturation, this proportionality holds true until complete absorption of the light.

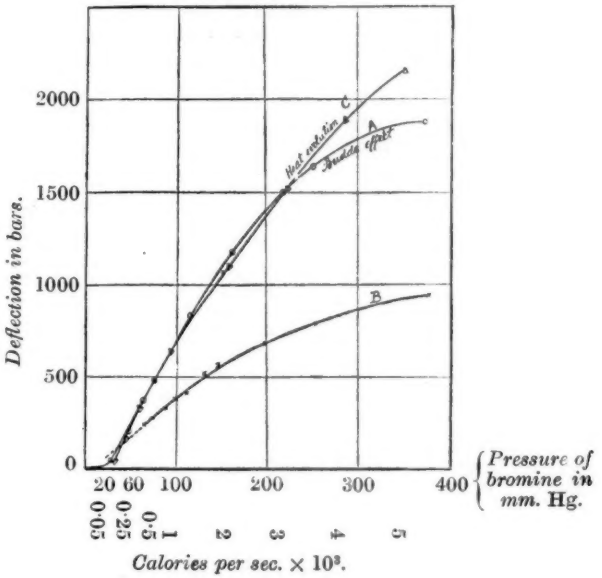
Over a certain pressure range the Budde effect increases proportionally to the increase in the partial pressure of the water vapour.

In Fig. 3 are plotted the Budde effects as functions of the partial pressures of bromine at the constant water-vapour pressures of 2·77 mm. (A) and 0·20 mm. (B), respectively, and at 40°, the distances of the lamp from the bulb being 21 and 32 cm., respectively. Above partial pressures of bromine of *ca.* 20 and 40 mm., respec-

tively, the curves follow the same course as those noted for the constant bromine–variable water-vapour pressure curves, *viz.*, the Budde effect is proportional to both the partial pressure of the bromine and of the water vapour. Such a relationship is most readily interpreted on the assumption that the photoactive constituent responsible for the Budde effect is a bromine hydrate of composition Br_2,H_2O in mass equilibrium with the reactants according to the equation

$$Br_2 + H_2O \rightleftharpoons Br_2,H_2O.$$

FIG. 3.

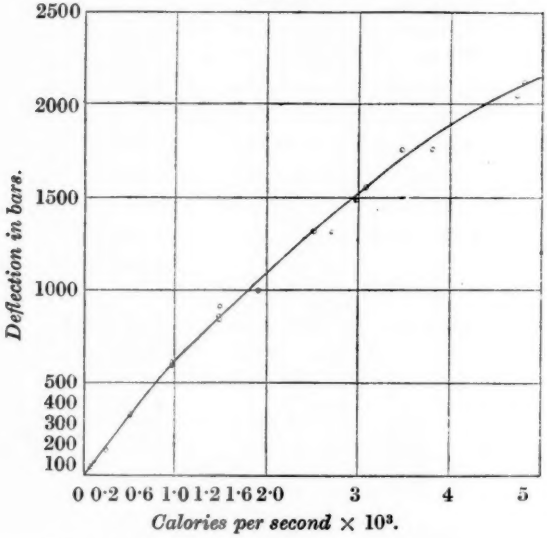


In the light of this hypothesis the convex form of the curve for low water-vapour pressure (Fig. 2) and the concave form of the constant water-vapour pressure curves at low bromine pressures (Fig. 3) are significant.

It is clear that when the partial pressures of water are low (below 0·005 mm.) the Budde effect rises more rapidly than we should be led to expect from application of the law of mass action to the bulk phase. If bromine hydrate were strongly adsorbed by the walls of the glass vessel, the surface concentration increasing with the partial pressure until a saturation maximum was attained at about 0·10 mm., the reason for this increase of the Budde effect at low partial pressures of water vapour and the convex form of the curve when the walls are dry would be clear. Again, if in the

presence of high pressures of water and low partial pressures of bromine the walls of the vessel are covered with water, the Budde effect will consequently be proportional to the bromine hydrate in the gas phase at the commencement, but will rise more rapidly as the pressure of the hydrate increases and displacement of the adsorbed water by the latter commences, thus explaining the initial concave form of the curves for low bromine and high water-vapour pressures. With low partial pressures of water (Fig. 3, curve B) it will be seen that the displacement of water from the surface by the hydrate commences at a lower partial pressure. After this initial curvature the curve rises in a linear manner proportional

FIG. 4.



to the quantity of bromine hydrate present both in the surface and the gas phases.

Such a view, which is advanced from a knowledge of the hygroscopic nature of glass and the convex and concave forms of the bromine–water-vapour pressure curves at low partial pressures, is greatly strengthened by careful analysis of the convex curve. The Budde effect is, according to this view, due to absorption of light by bromine hydrate which is present both in the bulk phase and on the surface of the glass. The curve at low partial pressures of water is thus the effect of both the bulk and the surface concentrations. The bulk concentration increases in a linear manner with increase in water-vapour pressure until the light absorption becomes great, and this portion contributes a Budde effect given

by the line oa (Fig. 2). The surface concentration at various partial pressures contributes a Budde effect given by the curve oB—oa. If this be the case, it should be capable of expression in the form of an adsorption isotherm. Since it is probable that the water vapour and hydrate layer is but one molecule thick, the partial pressures being far lower than those employed by McHaffie and Lenher (J., 1925, **127**, 1559), where multimolecular layers were formed, the Langmuir isotherm should be applicable :

$$x = ap/(1 + bp),$$

where x = the surface concentration of the hydrate or is proportional to the Budde effect in the surface, p = the partial pressure of the hydrate in the gas phase or is proportional to the concentration of water, and a and b are constants.

The prolongation of the rectilinear portion of the curve, where the surface is hydrate-saturated, intersects the ordinate at 1610 bars. This, then, is the limit to the Budde effect produced by the surface phase.

Hence when p is large, $x = a/b = 1610$,
for $p = 0{\cdot}0005$, $300 = 0{\cdot}0005a/(1 + 0{\cdot}0005b)$.
From which we obtain $b = 458$, $a = 7{\cdot}38 \times 10^5$.

The following table shows the calculated and the observed values (in bars) of the Budde effect in the surface phase for increasing water-vapour pressures.

Partial press. of H_2O (mm.).	x calc.	x obs.	Partial press. of H_2O (mm.).	x calc.	x obs.
$3{\cdot}9 \times 10^{-5}$	28·4	66	0·01	1320	1200
$2{\cdot}3 \times 10^{-4}$	154	226	0·03	1500	1500
$5{\cdot}0 \times 10^{-4}$	300	300	0·08	1573	1590
$5{\cdot}0 \times 10^{-3}$	1100	950			

Taking into consideration the difficulties of evaluating the actual values of the Budde effect for the initial portion of the curve, which is extremely steep, the agreement between the observed and the calculated values does not exceed the experimental error.

The bromine hydrate which is the photoactive constituent responsible for the Budde effect is thus present in the reacting system both on the walls of the containing vessel and in the homogeneous gas phase, the distribution between surface and bulk phases obeying the usual adsorption isotherm equation.

In order to confirm the view that even at low partial pressures of water vapour there was adsorbed on the walls of the containing vessel a relatively large quantity of hydrate even when the bulk concentration was low, the following experiment was devised.

A small horizontal cell 4 cm. long and 1·25 cm. in diameter with

plane glass ends was constructed. Inside the cell a round coverslip was placed in a vertical plane so that the light passed through the ends of the cell and through the coverslip; a gentle shaking of the cell permitted the coverslip to fall down so that the narrow circular beam of light now passed only through the ends of the cell and the gas phase. Behind the cell a small Moll thermopile was placed so as to obtain a measure of the radiation absorbed by the cell. In addition, the cell was connected to the glass gauge and bromine reservoir in the usual manner.

The following data were obtained on illumination with light passing the colour filters employed in the previous investigation.

Expt. 1.

Cell.	Gas in cell.	Thermopile galvo. deflection.		Budde effect.
Coverslip up.	Air.	22·27	2·04	nil
„ „	Bromine at 104 mm.	20·23		7—8 av. 7·5
Coverslip down.	„ „ „	21·15	1·12	4
„ „	Air.	22·27		nil

It will be noted that with air, the position of the coverslip did not affect the amount of light falling on the thermopile, indicating absence of scattering, reflection or absorption of the light due to the glass. When the coverslip was up, the light passed through four glass–gas interfaces and when down through but two such interfaces, the former producing a larger Budde effect and a larger light absorption. If the amount of hydrate in the homogeneous gas phase be denoted by x, producing a Budde effect, kx, and a light absorption, lx, and that on each glass–gas interface be denoted by y, producing effects ky and ly, respectively, we obtain the following relationships:

(*a*) From the Budde effect.

$$4y + x = 7{\cdot}5k \quad \text{and} \quad 2y + x = 4k,$$

whence

$$2y = 3{\cdot}5k \quad \text{and} \quad x = 0{\cdot}5k,$$

or 12·5% of the Budde effect is produced by hydrate in the gas phase and 87·5% produced by hydrate on the two flat ends of the cylinder.

(*b*) From the absorption of light.

$$4y + x = 2{\cdot}04l \quad \text{and} \quad 2y + x = 1{\cdot}12l,$$

whence

$$2y = 0{\cdot}92l \quad \text{and} \quad x = 0{\cdot}20l,$$

or 17·8% of the Budde effect is produced by hydrate in the gas phase and 82·2% produced by hydrate on the two flat ends of the cylinder.

A repetition of this experiment with a bromine pressure of 140 mm. with the same water-vapour pressure gave the following values:

	Coverslip up.	Coverslip down.
Absorption	3·06	1·75
Budde effect	12	7

whence we obtain the following percentages for the distribution of the hydrate :

	% In bulk phase.	% On surface phase.
From Budde effect	28	72
From absorption of light	25·3	74·7

As the concentration of hydrate is increased by elevation of the bromine pressure, the bulk concentration of hydrate increases more rapidly than the surface concentration, which, as shown in the previous experiments, finally approaches a surface saturation maximum. From Fig. 2 the percentage of the maximum Budde effect caused by the surface phase is 75, and that of the volume 25 under the experimental conditions.

In Fig. 3 the initial concave portion of the curve was attributed to the effect of the surface adsorption of water vapour which when present in large quantities could displace bromine hydrate when present in but small quantities, *i.e.*, at low partial pressures of bromine.

To confirm this view, both the light absorption and the Budde effect for the bromine in the small cell were determined for low and high partial pressures of water. If excess of water displaces the adsorbed bromine hydrate from the glass surfaces, we should anticipate that, in spite of the increase of the bromine hydrate in the bulk phase due to the addition of water, the removal of the bromine hydrate by displacement from the walls will cause a diminution in the total Budde effect. The following data were obtained :

Cell containing	Deflection for thermopile.	Budde effect.	Absorption.
Air	25·49	0	—
Bromine at 144 mm.	22·49	11	3·00
Bromine at 144 mm. and H_2O vapour at 18°	23·12	9	2·37

The diminution in the Budde effect on a very large increase in the partial pressure of water is clearly brought out.

Summary.

The Budde effect in bromine is shown to be proportional to both the partial pressure of bromine and of water vapour and is probably due to a photoactive bromine hydrate of composition Br_2,H_2O. This hydrate is strongly adsorbed by glass surfaces and the relationship between the concentration in the bulk and the surface phases can be expressed in the form of an adsorption iso-

therm. The hydrate may be displaced from glass surfaces by water. The Budde effect was not observed on illumination of moist bromine with light of wave-length longer than $\lambda = 5800$ Å.

THE LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, November 16th*, 1925.]

LXXXII.—*The Budde Effect in Bromine. Part II. The Kinetics of the Reaction and the Light Absorption of Wet and of Dry Bromine.*

By BERNARD LEWIS and ERIC KEIGHTLEY RIDEAL.

IN Part I evidence was presented for the view that the photo-active constituent responsible for the Budde effect in moist bromine is a bromine hydrate of composition Br_2,H_2O which is present both in the homogeneous gas phase and on the walls of the containing vessel. The adsorption isotherm equation was shown to be applicable to the partition of the hydrate between the two phases.

It was considered of interest to examine the properties of this bromine hydrate in more detail.

The Equilibrium Constant and Heat of Formation.

From a determination of the Budde effect at various temperatures the alteration of the equilibrium

$$Br_2 + H_2O \rightleftharpoons Br_2,H_2O$$

can be determined. The determinations were carried out with the apparatus described in the previous communication. A low partial pressure of water was employed so that the Budde effect was due almost entirely to the adsorbed bromine hydrate. The following values were obtained, t being the temperature of the bath, and K/K_p the deflection in scale divisions:

t	99°	81°	63°	41°	22°
K/K_p	86	95	106	122	140

The deflection decreases, or the equilibrium constant, K_p, where

$$K_p = [Br_2][H_2O]/[Br_2,H_2O],$$

increases, with elevation of the temperature.

Since an intense light was employed and the bromine hydrate concentration was low, the deflection is proportional to the concentration of the hydrate on the surface and may be employed in the van 't Hoff isochore to calculate the heat of formation.

Inserting the above values in the equation

$$2{\cdot}3 \log_{10} \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

we obtain the following values (in calories) for Q: $Q_{81°} = 1440$, $Q_{63°} = 1425$, $Q_{41°} = 1340$, $Q_{22°} = 1336$.

Since $Q_t = Q_0 + \beta T^2$, where $2\beta =$ the difference in specific heat of reactants and products, we obtain

$$\beta = 0{\cdot}0028 \text{ and } Q_0 = 1090 \text{ cals.}$$

Thus the heat change in the formation of the hydrate in the surface phase can be expressed as follows:

$$Br_2 + H_2O = Br_2,H_2O + 1090 \text{ calories.}$$

The magnitude of Q_0 is in agreement with expectations regarding the heat of formation of such an unstable compound; it is practically identical with the heat change on solution of bromine in water:

$$Br_2 \text{ (liq)} + H_2O \text{ (600 mols.)} \longrightarrow Br_2 \text{ aq} + 1080 \text{ calories.}$$

From a knowledge of the heat of reaction it is possible, with the aid of the approximation equation of the Nernst heat theorem, to calculate the value of the equilibrium constant.

Inserting the values $Q_0 = 1090$ (if there is a difference in the heat of formation in the surface phase and the bulk phase it cannot be very large, for the heat of formation is already so small. We may therefore without serious error assume 1090 cal. as the heat of formation in the bulk phase), $T = 313°$ K, $\Sigma\nu = 1$, and $\Sigma\nu C = 3$ in the equation

$$\log_{10} K_p = \frac{-Q_0}{4{\cdot}571T} + 1{\cdot}75\,\Sigma\nu \log T + \Sigma\nu C,$$

we obtain $\log_{10} K_p = 6{\cdot}61$ or $K_p = 4{\cdot}10 \times 10^6$ in atmospheres $= 3{\cdot}10 \times 10^9$ in mm.

From this value we find that with a partial pressure of bromine of 200 mm. and of water vapour of 10 mm. the partial pressure of the hydrate will be $0{\cdot}65 \times 10^{-6}$ mm., equivalent to a concentration of $3{\cdot}86 \times 10^{-11}$ g.-mol. per litre in the bulk phase.

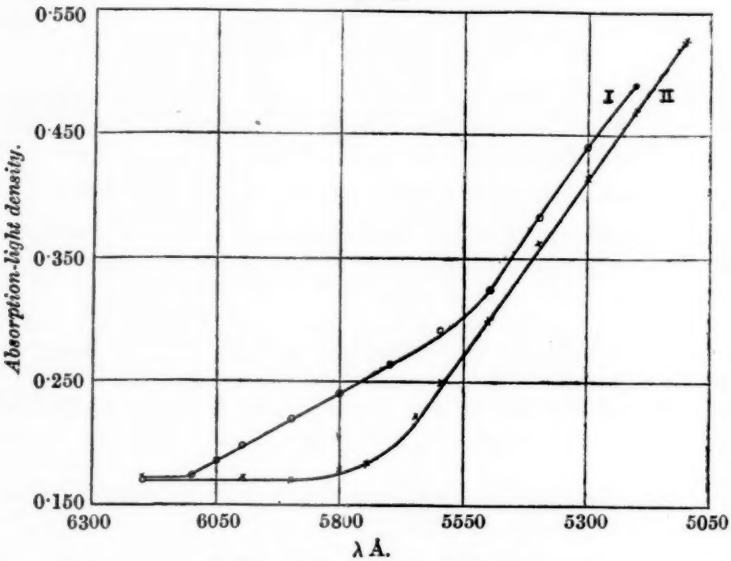
The increase of pressure on illumination has been taken as a measure of the equilibrium constant at various temperatures. Such a procedure is justified, since the Budde effect has already been shown to be proportional to the concentration of the hydrate and the large value of K_p for the equilibrium constant indicates that the equilibrium concentration of the hydrate is always so small that even large alterations in its concentration due to alteration in the temperature cannot affect the concentration of bromine or water, which may be regarded as constant.

The Absorption Spectrum.

If this small quantity of bromine hydrate is the photoactive constituent, it must possess properties different from those of dry bromine. An examination of the absorption spectra of wet and of dry bromine revealed interesting differences.

In Fig. 1 are plotted the absorption curves for wet and for dry bromine determined with the aid of a Nutting spectrophotometer (zero = 0·173), the dry bromine being retained in a clear quartz polarimeter tube which, previously to the admission of bromine,

FIG. 1.



I. *Wet bromine.* II. *Dry bromine.*

stored over phosphoric oxide for 9 to 10 months, had been thoroughly ignited whilst a high vacuum was maintained in the system.

The curves indicate that whilst ordinary bromine in wet vessels commences to show a definite absorption at $\lambda = 6100$ Å., the dry bromine shows no marked absorption before $\lambda = 5700$ Å. If light absorption is taken as a criterion of molecular excitation, the complex bromine–water requires an energy of excitation 3200 calories per g.-mol. less than that of dry bromine (2·05 volts compared with 2·20 volts) and it might be suggested that the catalytic effect of water vapour in many reactions may in part be due to the lower critical energy increment required for excitation of the complex hydrate.

Whilst the absorption of radiation by the hydrate results in the degradation of the radiant energy, dry bromine absorbs radiation of light of $\lambda = 5700$ Å. This light, however, does not reappear as thermal energy, for dry bromine shows no Budde effect. It must be concluded that such light which does not pass through the tube and is not degraded to heat must be either reflected or absorbed and re-emitted by the dry bromine molecules in the direction of the sides of the tube, *i.e.*, must be emitted as resonance radiation or fluorescence. In the presence of water vapour more light is absorbed and fluorescence would be reduced. The possible extinction of such fluorescence in dry bromine by water vapour would appear to have its counterpart in the extinction of fluorescent mercury by gases such as hydrogen and water vapour noted by Stuart (*Z. Physik*, 1925, **32**, 262) and the extinction of fluorescence by water vapour in hydrogen and oxygen mixtures noted by Baker. It would further suggest the emission and absorption of light from molecule to molecule in a dry gas until absorption by a hydrate molecule occurred as a mechanism for chain reactions. Several experiments were devised to detect the difference between the nature of the light emitted from the sides of narrow tubes containing wet and dry bromine respectively, down the axes of which narrow pencils of yellow light were passed. Whilst no quantitative data could be obtained, the light emitted from the dry bromine appeared somewhat yellower, *i.e.*, richer in the rays absorbed by bromine, than the reddish light from the wet tube.

The Stark–Einstein Law of Photoequivalence.

An attempt was made to establish the validity of the Stark–Einstein law of photochemical equivalence in the case of the Budde effect. The measurements of the absorption of energy by the reaction vessel containing bromine were made with a black-body radiation meter. The meter consisted of a flat black receiving bulb with compensator and aniline gauge and was calibrated by the method of internal electric heating with the aid of a small platinum spiral in the interior; the whole system being carefully lagged and preserved from any slight air currents which might affect either the steadiness or accuracy of reading. Due corrections were made for the resistance of the circuit and leading-in wires. The following calibration values were obtained:

Room temperature 20·2°. Reading in scale div.	Cal./sec.	Ergs per sec. per 10 div. $\times 10^{-4}$.
3·5	$5{\cdot}36 \times 10^{-4}$	6·42
4·7	$7{\cdot}73 \times 10^{-4}$	6·88
6·8	$1{\cdot}29 \times 10^{-3}$	7·93
10·7	$2{\cdot}55 \times 10^{-3}$	10

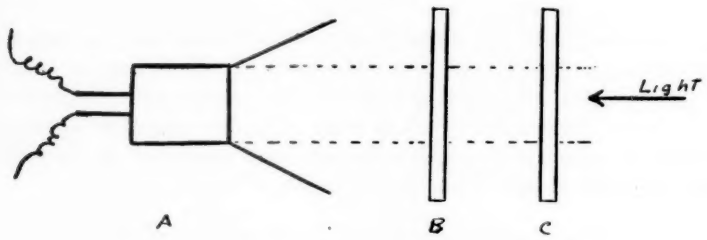
In a typical experiment with light between 5300—5700 Å. it was found that the bromine absorbed energy, as measured by the radiation meter, of $1{\cdot}53 \times 10^4$ ergs per second, yielding a Budde effect of 184·8 bars.

As has already been indicated, part of the light apparently absorbed by the bromine, *i.e.*, not transmitted to the radiation meter, is emitted from the sides of the tube in the form of fluorescence. It was necessary to find out how much of the energy of $1{\cdot}53 \times 10^4$ ergs per second was emitted as fluorescence, *i.e.*, apparently absorbed by dry bromine, and how much contributed to the Budde effect by absorption by the bromine hydrate. The following arrangement (Fig. 2) was accordingly devised to evaluate this fraction :

A. Moll thermopile.

B. A reaction vessel similar to C containing moist bromine at the same partial pressure, or air.

FIG. 2.



C. Reaction vessel containing either dry bromine in contact with phosphoric oxide, or air.

The two reaction vessels were of similar size and shape, both with plane and parallel sides immersed in a trough through which water from a thermostat was circulated. The point light lamp, water trough, collimator, and screens were used as heretofore. After the lamp had been so adjusted that a constant deflection was obtained on the Moll thermopile with the bulbs containing dry air, dry bromine was first admitted to bulb C at a partial pressure of 120 mm. The deflection on the thermopile was noted and moist bromine (saturated at 17°) admitted to B until the partial pressures of the bromine in the two bulbs were identical. The deflection was again noted and the bromine in the bulb C was replaced by dry air; the final determination of the radiation transmitted to the thermopile was then made. These operations were repeated, reversing the procedure in each case, and the following average readings were obtained :

B containing air / C containing dry bromine } 24·80 B containing dry air / C containing dry air } 25·43

B containing moist bromine / C containing dry air } 23·97.

These results indicate that the apparent absorption by dry bromine is represented by 0·63 division on the Moll thermopile, that by wet bromine by 1·46 divisions; or about 43·2% of the light apparently absorbed by the moist bromine is emitted again in the form of radiation, as it does not contribute to the thermal energy to which the Budde effect is due.

The areas under the absorption curves between wave-lengths 5400 Å. and 6100 Å. will give the percentage absorptions due to wet and to dry bromine (wet bromine absorbs up to 6100 Å.; the filter transmitted the red rays):

Area under dry curve = 3130. Area under wet curve = 6530.
% absorbed by dry Br_2 = 48. % absorbed by wet Br_2 = 52.

All the light absorbed by the unhydrated bromine in the wet bromine is not emitted as fluorescence from the sides of the vessel. A part of it is reabsorbed by the hydrated molecules and degraded into heat energy. What proportion is reabsorbed we have no means of determining from our data. It must be borne in mind that as far as the absorption spectra curves are concerned it makes no difference how much of the emitted light is reabsorbed, since only a small portion of this light, even if not reabsorbed, would find its way through the spectrophotometer.

Accordingly, of the $1{\cdot}63 \times 10^4$ ergs per second apparently absorbed, or not transmitted by the wet bromine, in the previous experiment, 56·8% is actually absorbed and 43·2% emitted as radiation, or $0{\cdot}926 \times 10^4$ ergs per second are absorbed. The mean wave-length of light employed was 5550 Å., for the energy distribution curve of the radiation passing through the filter was flat within the region 5300 Å.—5800 Å. or the mean quantum was $3{\cdot}53 \times 10^{-12}$ erg; the number of quanta actually absorbed by the bromine hydrate per second is accordingly $0{\cdot}926 \times 10^4/3{\cdot}53 \times 10^{-12}$ or $2{\cdot}62 \times 10^{15}$ quanta per second.

The Budde effect was 184·8 bars, corresponding to a heat evolution, as determined from the curve given in Part I, of $1{\cdot}26 \times 10^4$ ergs per second. If this heat is evolved by the conversion of quanta of magnitude $3{\cdot}53 \times 10^{-12}$ erg into kinetic energy in the decomposition or deactivation of the excited bromine hydrate molecules, we obtain as the number of molecules undergoing such a process of deactivation or decomposition per second $1{\cdot}26 \times 10^4/3{\cdot}53 \times 10^{-12}$ or $3{\cdot}57 \times 10^{15}$.

In the following table are the results of three different experi-

ments performed in the above manner. Figures in the third column are obtained by multiplying the calibration value in the previous table by 1·11 to allow for diffusive reflection of lampblack.

Exp.	Temp.	Manometer diff.	Total ergs per sec. not transmitted $\times 10^{-4}$.	Quanta per sec. absorbed by the hydrate $\times 10^{-15}$.	Budde effect in bars.	Ergs per sec. equivalent $\times 10^{-4}$.	Mols. per sec. decomposing $\times 10^{-15}$.	Mols. per quanta.
2	20·8°	2·28	1·63	2·62	184·8	1·26	3·57	1·36
3	20·9	2·43	1·73	2·78	186	1·30	3·68	1·32
4	20·2	1·73	1·24	2·00	149	1·01	2·82	1·41

These calculations were made under extreme conditions allowing for no absorption by the hydrate molecules of the re-emitted radiation from dry bromine. Taking this into account would bring the figures in the last column close to unity.

However, it will be noted from the data in the last column that the agreement between the number of quanta absorbed per second by the hydrate and the number of such molecules decomposing per second with the liberation of the energy of activation in the kinetic form is sufficiently close to show the validity of the Stark–Einstein law of photoequivalence in the case of the Budde reaction.

The Absorption Coefficient of the Hydrate.

On the hypothesis that the photoactive constituent is a bromine hydrate it is possible from a consideration of its concentration and the magnitude of the Budde effect, which is a measure of the light actually absorbed by the hydrate, to effect a determination of the absorption coefficient. The actual bulk concentration of hydrate for definite partial pressures of bromine and water can be determined only on the assumption that the concentration equilibrium of the reaction

$$Br_2 + H_2O \rightleftharpoons Br_2,H_2O$$

is not sensibly affected whether the water vapour and the hydrate are in the surface or bulk phases, an assumption which is only valid if the activity coefficients of the reactants do not change sensibly during adsorption, or that the change in the activity coefficient of the water on adsorption is the same as the change effected in this function of the bromine hydrate. Since the heat of formation of bromine hydrate is small, some measure of support is given to the latter hypothesis. We will therefore employ the value for K_p determined above as $3{\cdot}10 \times 10^9$ when expressed in mm. of mercury.

From the curves given in Fig. 2 (Part I of this investigation), in which the increase in Budde effect with increasing water-vapour pressure at a constant bromine pressure is plotted, it is seen that at a pressure of 0·0415 mm. of water and a pressure of 158 mm.

of bromine, a Budde effect of 115 bars was caused by the bromine hydrate in the gas phase, out of a total of 2140 bars (maximum deflection under the intensity of illumination employed).

Thus 5·4% of the light was absorbed by the bromine hydrate present in the gas phase, which was 2·35 cm. deep, or 94·6% would have been transmitted if no surface phase existed. The partial pressure of the hydrate in the gas phase can with the proviso indicated above be determined with the aid of the equilibrium constant or

$$[Br_2][H_2O]/[\text{Hydrate}] = 3{\cdot}10 \times 10^9 = 158 \times 0{\cdot}0415/[\text{Hydrate}],$$

whence the partial pressure of the hydrate is $2{\cdot}1 \times 10^{-9}$ mm. From Beer's law, $I_t = I_0 e^{-kcd}$, where I_0 is the entering light, I_t the transmitted light, c the concentration, d the thickness, and k the absorption coefficient of the hydrate, we obtain :

$$\log_e (I_t/I_0) = -kcd,$$

or $$2{\cdot}3 \log_{10} 0{\cdot}946 = -kcd = -k(2{\cdot}1 \times 10^{-9}) \times 2{\cdot}35,$$

whence $$k = 10{\cdot}7 \times 10^6.$$

In a similar manner, for a point where $P_{H_2O} = 0{\cdot}083$ mm. we find a Budde effect, in the gas phase, of 230 bars or 10·75% light absorption, whence $I_t/I_0 = 0{\cdot}8925$ and $k = 11{\cdot}4 \times 10^6$. For the low partial pressure of $P_{H_2O} = 0{\cdot}02$ mm. we find a Budde effect in the gas phase of 55 bars, equivalent to 2·57% light absorption or 97·43% light transmitted, whence $k = 9{\cdot}6 \times 10^6$. The mean value of the absorption coefficient is thus $10{\cdot}5 \times 10^6$.

It is interesting to compare this value with that obtained by Wood (*Physikal. Z.*, 1912, **13**, 353) for the absorption of the light ($\lambda = 2537$ Å.) by mercury vapour. He found that the intensity of this light was reduced by one-half by passage through a layer of mercury vapour 5 mm. thick and at a partial pressure of 10^{-4} mm. Inserting these values in the equation, we obtain

$$2{\cdot}3 \log_{10} 0{\cdot}50 = -k \times 10^{-4} \times 0{\cdot}5, \text{ whence } k = 0{\cdot}14 \times 10^6.$$

Thus the absorption coefficient of bromine hydrate in the spectral region which produces excitation is comparable in value with that of mercury vapour for its resonance line. On the hypothesis of Ornstein that the range of influence of a quantum of light is proportional to the square of the wave-length, the absorption coefficient of bromine hydrate for light of $\lambda = 5550$ Å. should be some four times that of mercury vapour.

Mechanism of the Budde Effect.

The first elementary process in a photochemical action is, as Stern and Volmer (*Z. Wiss. Photographie*, 1920, **19**, 275) were the

first to show, not the primary reaction but the excitation of the molecule by absorption of radiation. On the hypothesis that there exist in moist bromine both bromine and bromine hydrate molecules, the primary processes of light absorption are the conversion of these into active molecules:

$$Br_2 + h\nu \longrightarrow Br_2'. \quad Br_2,H_2O + h\nu \longrightarrow Br_2',H_2O.$$

We have seen that in the case of dry bromine no Budde expansion occurs, although light absorption undoubtedly takes place. The excited bromine molecules must thus lose their energy of excitation in the form of radiation. Whether the radiation emitted from an excited bromine molecule in the interior of the gas passes through the gas to the outer walls or undergoes a series of absorptions and emissions from numerous molecules in the operation of transfer of a quantum from the interior to the surface, or, again, whether the energy of the excited molecule is handed on by collision within the life of the excited molecule, *viz.*, 10^{-7} second, thus forming a chain, cannot be established with certainty. As in the case of the resonance line of mercury vapour, if the light is emitted from the bromine molecules as light of the same wave-length as the absorbed light, the course of the fluorescent light is interrupted in its path to the surface by its absorption by hydrate molecules, thus materially reducing the strength of the fluorescent light.

We have seen that only when a bromine molecule is moist, *viz.*, a bromine hydrate, do we obtain a Budde effect or conversion of the light energy into thermal energy. The frequency, ν, of any line may be considered as the sum $\nu = \nu^e + \nu^n + \nu^m$, where e is the electronic, n the oscillatory, and m the rotational quantum number (Mulliken, *Physical Review*, 1925). In absorbing a quantum, not only may the quantum level of the electron be changed, but also the oscillatory and rotational quantum energy levels. In the case of iodine at low pressures (Oldenberg, *Z. Physik*, 1923, **18**, 1), the molecule, without dissociating, can absorb and re-emit as a resonance spectrum an amount of energy five times the work of dissociation when it is illuminated by light of wave-length $\lambda = 1849$ Å. The explanation advanced is that the excitation energy is primarily employed in raising the electron system to a higher quantum state, whilst the oscillation and rotation energies are only altered by the coupling of their periods with those of the electron system. But we may have, in the case of the halogens, marked changes in the oscillation energy where the absorption of light alters the potential energy of the nuclei, thus altering the strength of chemical binding of the molecule. In the excited electronic state, the energy required for dissociation is less than in the normal state, and if the alteration

in the oscillation quanta is sufficient to cause the potential energy of the nuclei to become greater than the dissociation energy for the excited state the molecule will fly apart. There is indeed a correlation between a large change in oscillation quantum number and a considerable alteration of the strength of binding on excitation. As a measure of the strength of binding we can utilise, for qualitative estimates, the direction of the shading of the bands, which is an indication of change in the moment of inertia of the molecule. The band spectra of iodine investigated by Mecke (*Ann. Physik*, 1924, **71**, 104) show a convergence limit of the oscillation quantum states at 5000 Å. Wave-lengths, therefore, of 5000 Å. or less will dissociate iodine under certain conditions. The convergence limit for bromine has been placed by Franck (see Part I, *loc. cit.*) at about the same wave-length from the position of the long wave-length limits of the continuous spectra which are known.

The light used in this investigation being of considerably greater wave-length, dry bromine would not be expected to dissociate. That dissociation does not occur is proved further by the work of Ludlam (see Part I, *loc. cit.*), who found no Budde effect with dry bromine illuminated with ultra-violet light containing energy many times that necessary for dissociation.

It would appear that in the case of bromine hydrate the lowering of the critical energy increment for dissociation into atoms is very great. Dissociation may occur thus:

(1) $Br_2,H_2O + 51{,}500$ calories $= 2Br + H_2O + 4410$ calories,

where 51,500 calories is the energy of the radiation of wave-length employed in these experiments, some 4410 calories greater than the threshold value, as is confirmed by the commencement of absorption at 6100 Å. The recombination of the bromine and water to re-establish equilibrium gives rise also to the evolution of the heats of combination:

(2) $2Br = Br_2 + 46{,}000$ calories.

(3) $Br_2 + H_2O = Br_2,H_2O + 1090$ calories.

The same type of mechanism is given by the calculations of Christiansen (*Dansk Vid. Math. Phys. Medd.*, 1919, **1**, 14) for the reactions

$$Br + HBr + 43{,}700 \text{ calories} = Br_2 + H + 12{,}400 \text{ calories}$$

and $$HBr + 112{,}000 \text{ calories} = H + Br + 35{,}000 \text{ calories}.$$

Thus 47,090 calories appears to be close to the critical energy that must be absorbed by bromine hydrate before any Budde effect can be expected. The absorption of light of greater frequencies, for a given constant quanta absorption, merely increases

the heat effect on the right-hand side of the equation (1) and thus the Budde effect.

Summary.

The heat of formation of bromine hydrate is 1090 calories, comparable with the heat of solution of liquid bromine in water, whilst the equilibrium constant for the dissociation of bromine hydrate at 313° K is of the order of $3{\cdot}10 \times 10^9$. The absorption curves of wet and of dry bromine have been compared; marked absorption commences at $\lambda = 6100$ Å. for the wet and at $\lambda = 5700$ Å. for the dry gas; this corresponds to a lowering of the critical energy increment of excitation of 3200 calories. When corrected for the absorption and probable fluorescence of dry bromine, it is found that the Stark–Einstein law of photoequivalence is obeyed, a maximum of 1·41 molecules per quantum being obtained. The absorption coefficient of bromine hydrate for the spectral region employed is $10{\cdot}5 \times 10^6$, comparable with that obtained by Wood, $0{\cdot}14 \times 10^6$, for mercury vapour for the line $\lambda = 2537$ Å. A mechanism of excitation and decomposition of bromine hydrate molecules is advanced in explanation of the Budde effect.

Our thanks are due to Messrs. Brunner Mond for a grant which enabled us to purchase the apparatus necessary for this research.

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CAMBRIDGE. [*Received, November 16th*, 1925.]

LXXXIII.—*Studies of Valency. Part V. Absorption Spectra of Halogen and Sulphonic Derivatives of Camphor: Origin of the Ketonic Absorption Band.*

By THOMAS MARTIN LOWRY and GLYN OWEN.

1. *Scope of the Work.*

THE preceding paper on absorption spectra (Lowry and French, "Studies of Valency," Part IV, J., **1924**, **125**, 1921) dealt with the selective absorption of camphor and of some of its conjugated derivatives. Its principal feature was an experimental proof of the existence in camphorquinone and in methylenecamphor of two different types of conjugation, corresponding perhaps with the presence of "crossed" and of "concordant" polarities in these two compounds. In the present paper, these experiments have been extended to a series of halogen derivatives of camphor, for which data were required in connexion with measurements of rotatory

dispersion (J., 1925, **127**, 1260). The absorption spectra of some of these compounds had been plotted previously by one of us (Lowry and Desch, J., 1909, **95**, 807), but only by the old qualitative method of recording the last line transmitted through a given thickness of solution in sufficient intensity to leave a record on the photographic plate. These observations were therefore not sufficiently exact for a quantitative comparison, the ultimate result of which was to reveal the existence of a small discrepancy between the characteristic frequencies deduced from measurements of rotatory dispersion and those obtained by recording directly the maximum value of the molecular extinction coefficient.

The original purpose of the experiments demanded only a knowledge of the characteristic frequency of the band of selective absorption; but the data in Table I have an interest of their own, which exceeds that of the approximate coincidence of the frequencies deduced by the two methods referred to above. Thus, not only have we been able to draw more exact conclusions as to the effect of halogens on the familiar absorption band of the ketone, but the "general absorption" of the compounds, which can now be investigated just as accurately as their "selective absorption," has been found to present striking characteristics, especially with regard to the mutual influence of negative radicals (compare Part VII, following paper). In this way the observations have provided important clues as to the origin and significance of selective and general absorption in carbon compounds generally.

2. *Experimental Methods.*

Camphor-β-sulphonic acid, and four camphorsulphonates containing a halogen atom, were examined in aqueous solutions. The fifteen other halogen derivatives were all examined in *cyclo*hexane. This solvent was selected in order to conform as closely as possible to the conditions under which the rotatory dispersions of many of these compounds had been measured in benzene (J., 1925, **127**, 807). The choice of *cyclo*hexane as an alternative to benzene (which was not sufficiently transparent for measurements of absorption) was justified by the fact that some of its physical properties approximate very closely to those of benzene (Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, **104**, 430) and in particular that the wave-length of maximum absorption for a solution of camphor in *cyclo*hexane had been found to be the same as for a thin film of camphor in benzene (Lowry and French, J., 1924, **125**, 1924). Apart from these considerations, however, *cyclo*hexane has proved to be a good solvent for measurements of absorption, since, although unpurified specimens are not very transparent, and may even exhibit an absorption band,

the material can be purified readily by repeated shaking with 100% sulphuric acid on a mechanical shaker. When washed with water and distilled, it was then found to be transparent to about 2200 Å.U., which is approximately the limit of transmission of the calcite of the ultra-violet spectrophotometer.

The fifteen halogen derivatives of camphor and the five sulphonates had all been purified by crystallisation, and in most cases the samples had already been used for measurements of rotatory dispersion.

The methods of measurement were the same as in Part IV of this series of papers, absolute values being recorded for the "molecular extinction coefficients" at different wave-lengths up to the limit of transparency of the solution. As a rule, about 60 measurements were made with each compound, at concentrations ranging from $M/4$ to $M/400$; but the experimental points were too numerous to be inserted in the figures, except in one case (Fig. 7), where the range of wave-lengths and intensities made it possible to plot the data on a larger scale.

3. *Summary of Experimental Results.*

The present series of observations has proved that, whilst the presence of a halogen influences both the selective and the general absorption of the compounds, and affects these two properties in a somewhat similar manner, the two influences are sufficiently independent to produce large variations in the "persistence" of the band,* *i.e.*, in the relative separation of the accessible band of "selective" absorption and the inaccessible band of "general absorption" as measured by the depth of the trough between them. The experimental results, which are summarised in Table I, may therefore be discussed most conveniently under these two headings.

(*a*) *Selective Absorption.*—The principal results are as follows:

(i) The general proposition, that the position of the ketonic band is largely independent of the nature of the ketone, is confirmed, since the wave-length of maximum absorption ranges only from 2880 Å.U. in camphor to 3230 in $\alpha\alpha'$-dibromocamphor. The intensities also cover only a small range from $\log \varepsilon = 1{\cdot}4$ to $2{\cdot}0$. This is in marked contrast with the conjugated systems examined in Part IV, where the value of $\log \varepsilon$ rose from $1{\cdot}4$ in camphor to $4{\cdot}3$ in benzylidenecamphor.

(ii) A halogen in the α-position produces a marked "intensification" of the selective absorption, since it increases both the wave-length and the maximum extinction coefficient of the ultra-

* It is therefore unlikely that the general absorption of these compounds is a mere harmonic of the selective absorption.

TABLE I.

Selective and General Absorption of Halogen and Sulphonic Derivatives of Camphor.

No. of curve.	Substance.	Selective absorption. Maximum. λ max.	Maximum. log ε (max.).	Minimum. λ min.	Minimum. log ε (min.).	Persistence log ε (max.). −log ε (min.).	General absorption λ for log ε = 1·5.	General absorption log ε for λ = 2500.
	(a) *In cyclohexane.*							
I.	Camphor.	2880	1·45	<2327	<−0·26	<1·72	None at 2400 Å.U.	
II.	α-Chlorocamphor.	3050	1·72	2510	0·67	1·05	<2300*	0·68
	α′-Chlorocamphor.	3060	1·75	2550	0·94	0·81	<2300*	0·97
III.	α-Bromocamphor.	3100	1·95	2700	1·20	0·75	2590	1·83
	α′-Bromocamphor.	3120	1·95	2720	1·26	0·69	2530	1·96
IV.	β-Bromocamphor.	2930	1·39	2750	0·98	0·41	2370	1·12
V.	αα′-Dichlorocamphor.	3100	1·82	2570	0·22	1·60	2400	0·40
VI.	αα′-Bromochlorocamphor.	3150	1·84	2840	1·57	0·27	†	2·45
VII.	αα′-Dibromocamphor.	3230	1·88	2970	1·74	0·14	†	2·86
VIII.	α-Chloro-β-bromocamphor.	3060	1·67	2600	0·73	0·94	2400	1·3
IX.	α-Bromo-β-chlorocamphor.	3080	1·87	2690	1·40	0·47	2630	1·9
X.	αβ-Dibromocamphor.	3080	2·03	2700	1·46	0·57	2680	2·5
XI.	απ-Dichlorocamphor.	3080	1·68	2590	0·40	1·68	2370	0·5
XII.	α-Bromo-π-chlorocamphor.	3150	2·01	2610	0·59	1·42	2490	1·45
XIII.	απ-Dibromocamphor.	3120	2·05	2670	1·09	0·96	2590	1·83
	α′π-Dibromocamphor.	3090	2·02	2680	0·80	1·22	2560	1·85
	(b) *In water.*							
XIV.	Camphor-β-sulphonic acid.	2850	1·54	2390	0·50	1·04	2300	‡
XV.	Potassium α-chlorocamphor-β-sulphonate.	3000	1·59	2510	0·50	1·09	2300	0·51
XVI.	Potassium α-bromocamphor-β-sulphonate.	3030	1·93	2640	1·39	0·54	2600	1·90
XVII.	Ammonium α-chlorocamphor-π-sulphonate.	3030	1·85	2660	1·00	0·85	2500	1·50
XVIII.	Ammonium α-bromocamphor-π-sulphonate.	3020	2·09	2630	1·50	0·59	2630	1·90

* In these compounds, the general absorption is very weak and log ε does not rise to 1·5 within the limits of our experiments; the value of λ corresponding to log ε = 1·5 could therefore only be deduced by extrapolation.

† In these two compounds, where the general absorption is very strong, the molecular extinction coefficient falls to a minimum (at log ε = 1·6 and 1·75 respectively), and then begins to rise again towards the crest of the band of selective absorption, but it never falls as low as log ε = 1·5.

‡ In this compound, where the general absorption is very weak, the band of selective absorption extends to a minimum at about 2400 A.U.; the general absorption does not begin, therefore, until the wave-length is already less than 2500 Å.U.

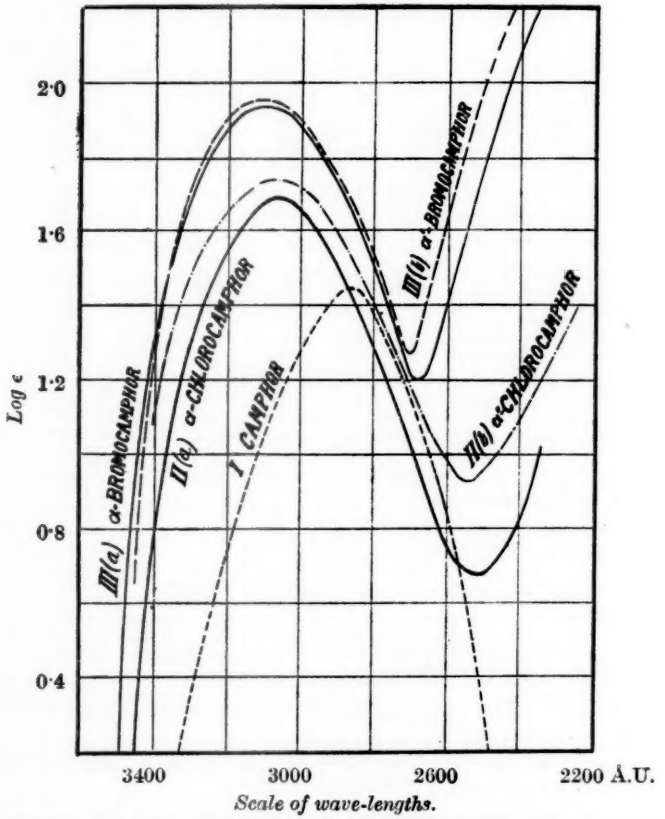
violet band (Fig. 1). The influence of an atom of bromine in the β-position is, however, almost negligible, since an insignificant increase of wave-length is balanced by an equally unimportant diminution in the maximum extinction coefficient (Fig. 7). The conclusion reached in an earlier paper (J., 1909, **95**, 817) that, whilst a halogen atom in a α-position produces an " intensification " of the band, an atom of bromine in the β- or π-position has a " repressive action," is therefore no longer valid when applied to the selective absorption alone instead of to the " persistence " of the band.

(iii) The data for the αβ- and απ-derivatives (Figs. 3 and 4)

confirm the conclusion that an atom of bromine in the β- or π-position produces only negligible changes in the wave-length and penetration of the band, and certainly has no " repressive " action.

(iv) The most striking intensification of the selective absorption is seen in the αα′-dihalogen derivatives (Fig. 2). In this group of

FIG. 1.

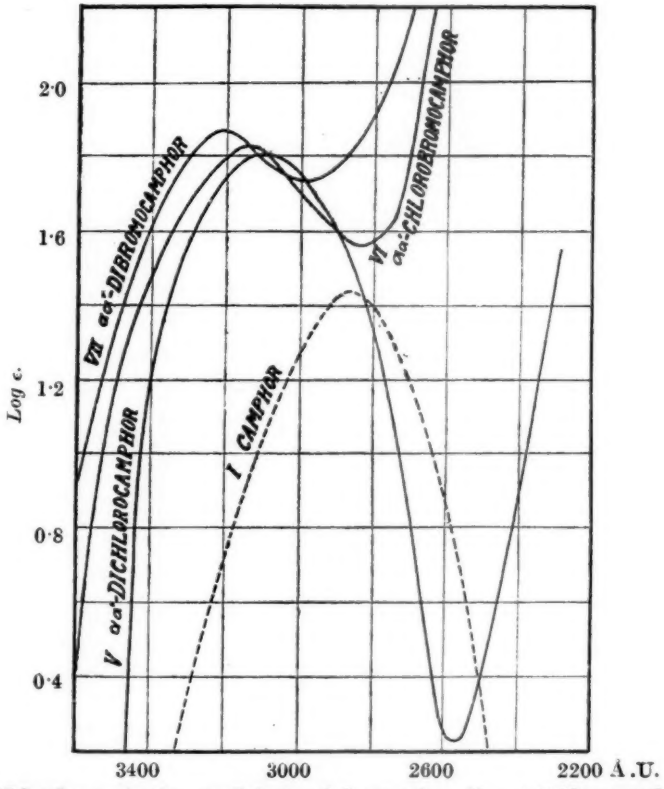


Molecular extinction coefficients of **I** *camphor,* **II**(*a*) *α-chlorocamphor,* **II**(*b*) *α′-chlorocamphor,* **III**(*a*) *α-bromocamphor,* **III**(*b*) *α′-bromocamphor in* cyclo*hexane.*

compounds the progressive replacement of chlorine by bromine is accompanied by a progressive increase in the wave-length of the band, whilst the maximum extinction coefficient remains practically constant at a value midway between those recorded for a single atom of chlorine or bromine in the α-position. On the other hand, a similar replacement of chlorine by bromine in the αβ-series (Fig. 3) produces a progressive increase in the value of the maximum

extinction coefficient, which is not accompanied by any marked change of wave-length. These two figures therefore recall, but in a much less striking form, the contrast between the optical effect of the two types of conjugation recorded in Part IV. In the $\alpha\pi$-series (Fig. 4), the principal contrast is between the α-chloro- and the α-bromo-compounds. Thus $\alpha\pi$-dichlorocamphor gives a band in

FIG. 2.

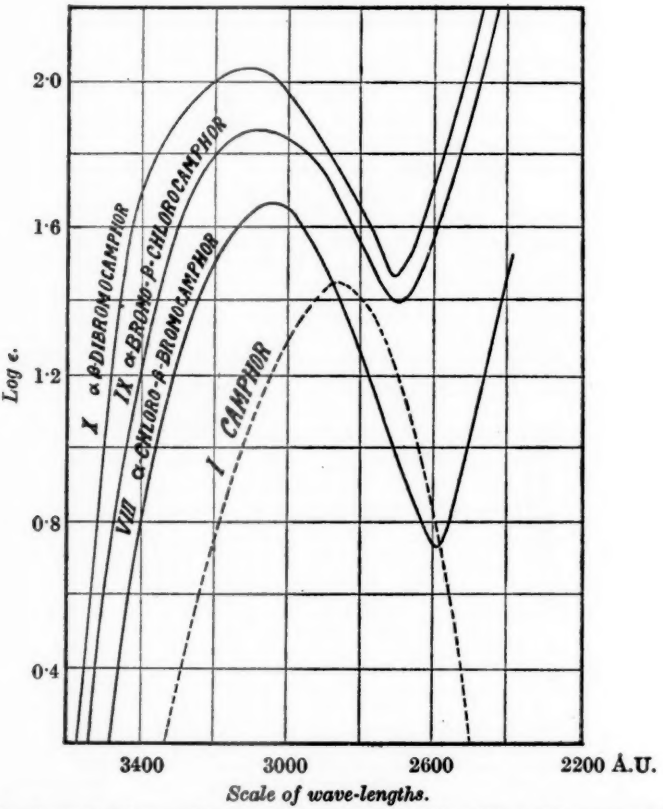


Molecular extinction coefficients of I *camphor,* V *αα'-dichlorocamphor,* VI *αα'-chlorobromocamphor,* VII *αα'-dibromocamphor in* cyclo*hexane.*

very much the same position as in α-chlorocamphor itself; and in the same way $\alpha\pi$- and $\alpha'\pi$-dibromocamphor (which give almost identical curves) and π-chloro-α-bromocamphor resemble α-bromocamphor very closely, although the introduction of a halogen atom in the π-position appears to produce a minute increase both in the wave-length and in the maximum value of the extinction coefficient of the bromo-compounds.

(v) The influence of a sulphonic group in the β- or π-position is almost negligible, like that of a halogen atom in either of these positions. Thus in Reychler's camphor-β-sulphonic acid (Fig. 5) a small increase of intensity is balanced by a small decrease of wave-length, just as in β-bromocamphor (Fig. 7) a small decrease of intensity was balanced by a small increase of wave-length. Similar

FIG. 3.



Molecular extinction coefficients of I *camphor*, VIII *α-chloro-β-bromocamphor*, IX *α-bromo-β-chlorocamphor*, X *αβ-dibromocamphor in* cyclo*hexane.*

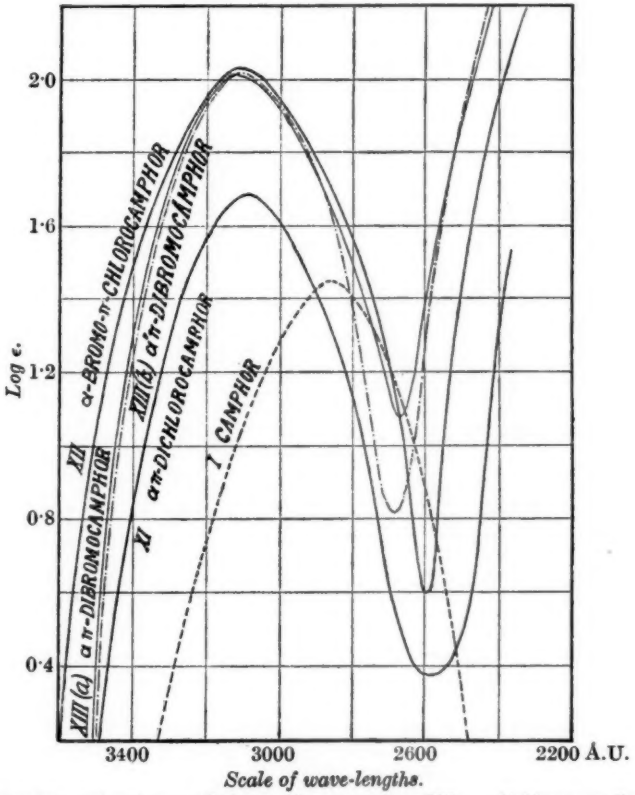
statements apply to the αβ- and απ-chloro- and bromo-sulphonates, where the introduction of the sulphonic group produces only small changes in the wave-length and intensity of the band of α-chloro- and α-bromocamphor.

(*b*) *General Absorption.* For the purpose of comparing general absorptions, we have chosen, quite arbitrarily, a standard wave-length, $\lambda = 2500$ Å.U., and a standard absorptive power, log $\varepsilon =$

1·5, and have recorded in Table I the wave-length at which the standard absorptive power is attained, and the absorptive power at the standard wave-length. The principal experimental results are as follows :—

(i) We have obtained complete confirmation of the recent observation of Lowry and French (J., 1924, **125**, 1924) that a solution of

FIG. 4.



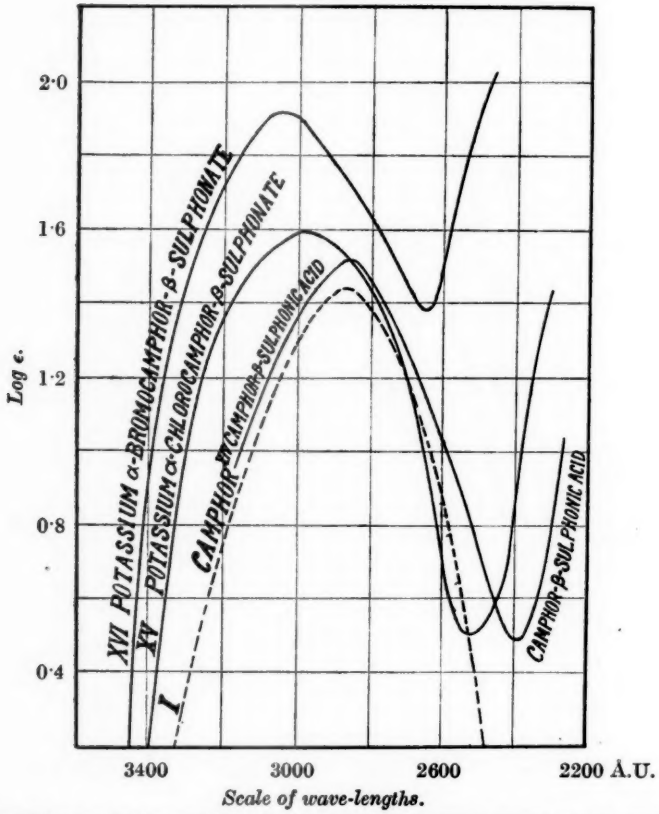
Molecular extinction coefficients of* I *camphor*, XI *απ-dichlorocamphor*, XII *α-bromo-π-chlorocamphor*, XIII (*a*) *απ-dibromocamphor*, XIII (*b*) *α'π-dibromocamphor in* cyclo*hexane.

camphor in *cyclo*hexane shows no general absorption up to the limits of our present methods of measurement. It is therefore impossible to record the persistence of the band, except by stating that it must be greater than 1·7.* It is indeed a noteworthy fact that, whereas

* In the same way, V. Henri found (*Ber.*, 1913, **36**, 3627) that acetone shows no general absorption up to 2144 Å.U., although the band had already persisted through a range of 2·0 in log ϵ, *i.e.*, over a range of intensities of 100 : 1.

the earlier methods of measurement always indicated the existence of a real or fictitious general absorption in every solution that was examined, we have failed completely in our attempts to detect by the quantitative method any trace of a general absorption in camphor itself when dissolved in *cyclo*hexane, although we have been able to

FIG. 5.



Molecular extinction coefficients of I *camphor* (*in* cyclo*hexane*), XIV *camphor-β-sulphonic acid* (*in water*), XV *potassium α-chlorocamphor-β-sulphonate* (*in water*), XVI *potassium α-bromocamphor-β-sulphonate* (*in water*).

reach the end of the band of selective absorption in all the twenty derivatives which were examined in the course of the present research, as well as in camphor itself when dissolved in alcohol (Lowry and French, *loc. cit.*). From the experimental point of view, it is a remarkable experience to find that a relatively strong solution of camphor, containing about 8 grams in 100 c.c., which extinguishes almost the whole of the ultra-violet spectrum from

3400 Å.U. onwards, becomes transparent again at about 2400 Å.U., and transmits with equal intensity all the remaining lines of the iron arc to 2327 Å.U.*

(ii) After camphor, the smallest general absorption was observed in camphor-β-sulphonic acid (Curve XIV), but, as the acid was examined in aqueous solution, the general absorption was easily observed, by reason of the exceptional transparency of the solvent. The minimum lies just beyond 2400 Å.U., but is followed by a very rapid increase, so that the general absorption was already almost level with the maximum of selective absorption (at $\log\varepsilon = 1{\cdot}54$) when the last readings were taken at about 2327 Å.U., in the clear aqueous solution. Apart from camphor, this compound was the only one in which the standard wave-length, $\lambda = 2500$ Å.U., selected for the comparison of general absorptions, fell within the limits of the band of selective absorption.

(iii) Although chlorine is not greatly inferior to bromine in its ability to intensify the selective absorption of camphor, it is relatively impotent in producing general absorption. Thus, apart from camphor and camphor-β-sulphonic acid, the only compounds in which the absorptive power did not reach the standard value of 1·5 within the limits of our experiments were the α- and α′-chlorocamphors (Curves II, *a* and *b*). Again, αα′-dichlorocamphor (Curve V), where the growth of general absorption is much more rapid than in the monochlorocamphors, has an exceptionally deep minimum at $\log\varepsilon = 0{\cdot}22$; and the persistence of the band, $\log\varepsilon$ (max.) $-$ $\log\varepsilon$(min.) $= 1{\cdot}60$, is greater than in any compound of the series except camphor itself, where it exceeds 1·72 (Lowry and French, *loc. cit.*, p. 1925), and απ-dichlorocamphor (Curve XI), where the general absorption only begins to be perceptible at a wave-length of about 2600 Å.U., after the band has attained a persistence of 1·68.

(iv) Bromine, on the other hand, which produces a strong general absorption even in α-bromocamphor, becomes extremely efficient in this respect when reinforced by an atom of chlorine or bromine in the other α-position. Thus, the general absorption at the standard wave-length of 2500 Å.U. *increases* from $\log\varepsilon = 1{\cdot}83$ in α-bromocamphor to 2·45 in αα′-chlorobromocamphor and to 2·86 in αα′-dibromocamphor. At the same time, as a result of the increase of general absorption, the persistence of the band *decreases* from 0·75 in α-bromocamphor to 0·3 in αα′-chlorobromocamphor and to 0·1 in αα′-dibromocamphor (Fig. 2). The general absorption in αα′-di-

* The fact that even this very "clean" band attains a width of 1000 Å.U. in solutions of only moderate concentration will explain why accurate measurements of rotatory dispersion can only be made for wave-lengths much greater than that of the crest of the band.

bromocamphor is indeed so great that at 2900 Å.U. it is already twice as strong as that corresponding with the maximum of the camphor band at the same wave-length. It is, therefore, only because the camphor band has been displaced by about 350 Å.U. in the direction of longer wave-lengths that the dibromo-derivative is able to exhibit a selective absorption at all: apart from this, nothing but a "step-out" would be observed in the curve.

(v) The reinforcement of the general absorption of α-bromocamphor by a second halogen in the β-position is comparatively small. Thus the general absorption remains practically stationary on passing from α-bromocamphor, where $\log \varepsilon = 1{\cdot}83$ at 2500 Å.U., to αβ-bromochlorocamphor, where $\log \varepsilon = 1{\cdot}90$, although this number rises to 2·5 in αβ-dibromocamphor. In the case of the π-compounds,* the general absorption actually *falls* from $\log \varepsilon = 1{\cdot}83$ at 2500 Å.U. in α-bromocamphor to 1·45 in απ-bromochlorocamphor, and remains stationary at 1·83 in απ-dibromocamphor. A sulphonic group in the β or π-position is also practically without influence in augmenting the general absorption of α-bromocamphor, since the value of $\log \varepsilon$ is only increased from 1·83 at 2500 Å.U. in α-bromocamphor to 1·90 in the two bromocamphorsulphonates.

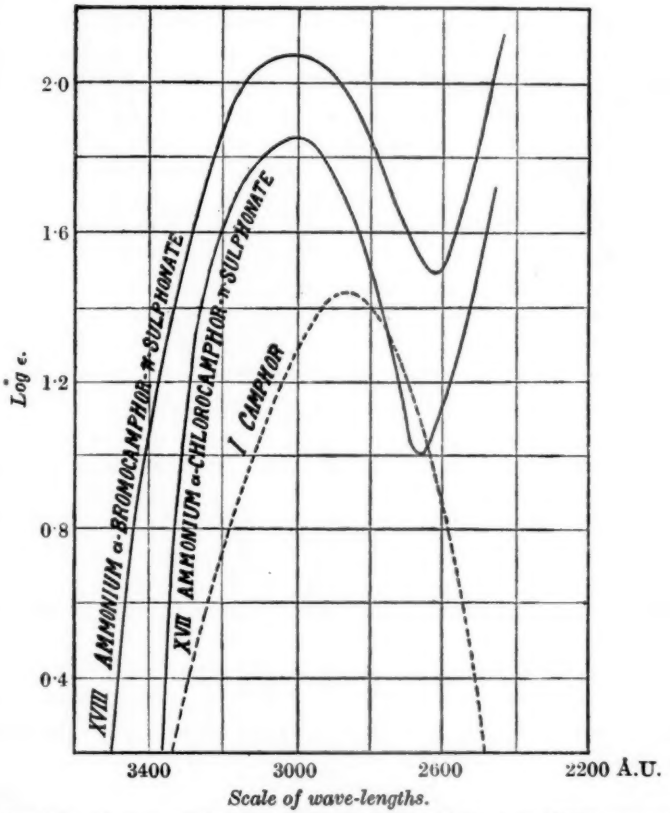
4. *Superposition of Selective and General Absorption.*

In accordance with the usual behaviour of negative radicals, halogens in the contiguous α-position have been found to augment the selective absorption of the ketonic group. Conversely, one must suppose that the ketonic group augments the power of the contiguous α-halogen atom to develop a general absorption, just as it increases the readiness with which reduction or reverse substitution takes place. In these cases, therefore, any superposition of general and selective absorption by mere addition would be out of the question, since it would ignore the known mutual influence of the negative atoms. This mutual influence diminishes, however, as the distance between the negative atoms is increased; and in β-bromocamphor the band of selective absorption is very similar to that of camphor itself, showing that one of the two mutual influences (namely, that of the halogen upon the ketonic group, but not necessarily that of the ketonic group upon the halogen) has become almost negligible. We have therefore attempted to reproduce the absorption curve of β-bromocamphor by superposing the general absorption of a compound containing the group $-CH_2Br$ (see Part VII) on the selective absorption of camphor itself. The general absorption of *one* molecular proportion of methyl bromide was found

* Anomalies in the optical properties of the π-derivatives have already been noted and discussed (J. 1925, **127**, 1504).

to be too small, whilst that of *half* a molecular proportion of methylene bromide or of ethylene bromide was too great, on account of the excessive mutual influence of the two halogens. Finally, by using a mixture of one molecular proportion of camphor with half a molecular proportion of trimethylene bromide (in which the two negative

FIG. 6.



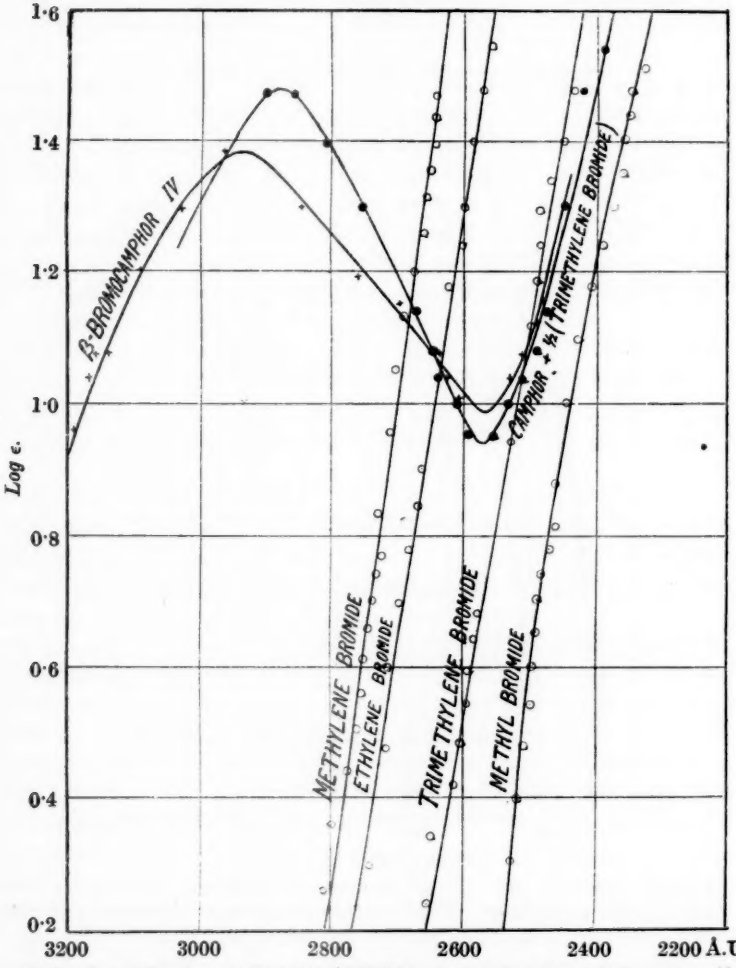
Molecular extinction coefficients of I *camphor in* cyclo*hexane,* XVII *ammonium α-chlorocamphor-π-sulphonate,* XVIII *ammonium α-bromocamphor-π-sulphonate in water.*

atoms are separated by three intermediate atoms of carbon, just as in β-bromocamphor), we have obtained an absorption curve (Fig. 7) which pursues very much the same course as that of β-bromocamphor, although it is not identical with it. In this way the validity of the principle of superposition of general and selective absorptions appears to be sufficiently established, whilst the theory which assigns the selective absorption to the >CO group and the

general absorption to the $>C$ Br group (see following paper) receives a direct experimental confirmation.

In addition to the absorption curve for β-bromocamphor, and the

FIG. 7.



Molecular extinction coefficients of IV *β-bromocamphor in* cyclo*hexane. Also of methyl, methylene, ethylene, and trimethylene bromide and of a solution of camphor with half a molecular proportion of trimethylene bromide in* cyclo*hexane.*

curve for a mixture of camphor and trimethylene bromide, Fig. 7 shows the curves of general absorption for solutions of methyl, methylene, ethylene and trimethylene bromides in *cyclo*hexane, the curves plotted in Part VII being for solutions in alcohol. On account

of the narrower range of wave-lengths and intensities which it covers, this diagram was plotted on twice the scale of Figs. 1 to 6; it was therefore possible to insert, without overcrowding, all the experimental points on which the curves were based.

5. Auxochromic Influence of Alkyl Radicals and of Halogens.

Bielicki and Henri (*Ber.*, 1913, **46**, 3627) and Rice (*Proc. Roy. Soc.*, 1915, *A*, **91**, 76) have shown that the absorption band of acetone is displaced towards the visible region when the hydrogen atoms are replaced by alkyl groups. Thus according to Rice "the shifts obtained in the successive substitution of the three α-hydrogen atoms are 23, 50, and 30 Å.U." for the first methyl, and the total shift of 103 units is doubled ($\lambda = 2747 \rightarrow 2850 \rightarrow 2950$ Å.U.) when the three hydrogens of the second methyl group are also replaced. On the other hand, Henri finds that a shift *in the same direction* occurs when the whole methyl group is replaced by hydrogen, since aldehydes give a band of longer wave-length and smaller intensity than ketones, in addition to showing a much stronger general absorption.

In order to determine the influence of halogens (and of negative radicals generally) on the absorption spectra of the ketones, it is convenient to take camphor instead of acetone as the parent compound, since the liquid halogen derivatives of acetone are less easy to prepare and purify than the alkyl derivatives (which are easily synthesised) and are in every respect inferior to the analogous compounds of the camphor series, where crystalline products are available in large numbers, and with the substituent in four different positions, namely, α or α′, β and π. It is a mere accident of nomenclature that in the α- and α′-derivatives of camphor the substituent is attached to a carbon atom in the "α" position relative to the ketonic group, and that in the case of the β-derivatives we can now assign the substituent to a methyl group of which the carbon atom is in a "β" position relative to the ketonic group (Lowry and Burgess, J., 1925, **127**, 279). In the π-compounds, the substituent is attached to a carbon atom in a "γ" position relative to the ketonic group, although it can also be reached by a longer route which would make it a "δ" carbon atom. It is therefore possible, by working in the camphor series, to compare the effect on the selective absorption of the ketonic group of introducing a negative substituent in an α-, β- or γ-position. The fact that the camphor nucleus is relatively complex is not a matter of great importance, since we have no reason for supposing that the influence of a negative group depends on the *shape* of the chain of atoms through which it is transmitted. It is, however, important to remember that there is

already evidence to show that the optical properties of the π-derivatives are sometimes abnormal (Richards and Lowry, J., 1925, **127**, 1504).

With these facts in mind, the experimental data given above can be summarised by saying that, whilst the general absorption is influenced profoundly by the introduction of a negative group *in any position in the molecule*, the selective absorption is influenced strongly by a halogen atom only when this occupies a contiguous α-position, the effect of a halogen or of a sulphonic group in the more distant β- and γ (π)-positions being negligible. Thus the increment for a single atom of bromine in the α- or α′-position is about 200 Å.U. (mean of 220, 240, 180, 150), and for a single atom of chlorine about 160 Å.U. (mean of 170, 180, 150, 130), when the other α-position is occupied by hydrogen; and it is about 120 Å.U. for bromine and 50 Å.U., for chlorine, when the other α-position is already occupied by a halogen. For a halogen in the β-position, the increments are − 20, + 50, + 10, − 20 Å.U. and for a halogen in the π-position, + 30, + 50, + 20, − 30 Å.U. A comparison with Rice's observations shows that the increments for two α-atoms of chlorine, or for a single α-atom of bromine, in camphor is already larger than for six α-methyls in acetone.

6. *Origin of the Ketonic Band.*

At the time when the earlier observations of absorption spectra were made (J., 1909, **95**, 807, 1340; 1910, **97**, 899, 905) it was thought that selective absorption was due to an oscillation in the molecule of the same period as that of the absorbed light. The experiments then described showed, however, that the ketonic band could not be due to the "isorropesis" or intramolecular oscillation of a mobile hydrogen atom, since bands were developed by many compounds which were incapable of undergoing isomeric change in the manner suggested. The conclusion was therefore drawn that "the camphor band is evidently in some way a function of the ketonic group," but that "it is not at all easy to say in what way the group acts in promoting the formation of the band."

This problem has, however, been simplified considerably by recent developments in physical optics, which lead us to ascribe the absorption, not to an intramolecular vibration, but to the presence of a system which when activated by light can take up energy quanta of suitable magnitude. On inquiry amongst physicists, we find that the ultra-violet ketonic band cannot be attributed to activation of the nuclei of the carbon and oxygen atoms relatively to one another, since this would give bands in the infra-red region; nor can it be due to the ionisation of the unshared electrons of the oxygen

atom (*all* the carbon electrons are shared), since the ionisation potential for oxygen corresponds with a wave-length far out in the Schumann region. The ketonic band can therefore only be attributed to an activation of the valency electrons of the double bond which forms the link between carbon and oxygen.

These valency electrons differ from the others in being simultaneously under the control of two nuclei, A and B. They can therefore be raised to a higher energy level relatively to A, or to B, or to A and B simultaneously. If A is carbon and B is oxygen (or in general if A is a less " negative " element than B), it will be easier to activate the valency electrons relatively to A than relatively to B. The effect will be to produce a " polar activation " of the double bond, since the valency electrons which absorb the light will be displaced from carbon towards oxygen, a process which (if continued far enough) would culminate in the ionisation of one link of the bond, and the conversion of the " non-polar " into a " semi-polar " double bond, as indicated by the scheme $>C=O \rightleftharpoons >\overset{+}{C}-\overset{-}{O}$.

The theory of polar activation, now used to explain the absorption of light by the unsaturated carbonyl radical, corresponds closely with the explanation given by Norrish (in Part III of this series of papers, J., 1923, **123**, 3006) of the arrest of the interaction of ethylene with bromine or chlorine, when enclosed in a vessel lined with paraffin wax, *i.e.*, that the interaction depends on a " polar activation " of the olefine and halogen, which can only be brought about at a polar surface. It should also be noted that, whilst semi-polar double bonds are permanent in the systems $>SO$, $>NO$, and $>PO$, they are not stable in $>C=C<$ or $>C=O$ (Sugden, J., 1925, **127**, 1525); they are, therefore, available as unstable or activated forms of the molecule in order to account for phenomena such as those discussed above.

The views now set out in reference to the utilisation of the energy absorbed by double bonds in unsaturated compounds could obviously be extended to single bonds; but since these are usually much more stable than double bonds, the quanta of energy required to activate them must be much larger, and the wave-lengths much smaller, than in the case of the ketonic band, corresponding, for instance, with a frequency in the Schumann region of the spectrum. Since this region is still inaccessible to our present methods of investigation of absorption spectra, saturated compounds generally give rise only to " general absorption."

7. *Summary.*

(*a*) Quantitative data are given for the general and selective absorption of twenty halogen and sulphonic derivatives of camphor.

(*b*) Halogen atoms in the α-position intensify both the general and the selective absorption of camphor; but halogen atoms and sulphonic groups in the β- or π-position are relatively impotent in increasing the selective absorption of the ketone, although they may contribute substantially to its general absorption.

(*c*) The origin of the ketonic band is discussed.

We wish to acknowledge our indebtedness to the University of Wales for a Fellowship Grant which has enabled one of us (G.O.) to take part in this work.

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CAMBRIDGE. [*Received, November 19th*, 1925.]

LXXXIV.—*Studies of Valency. Part VI. General and Selective Absorption of Halogen Derivatives of Methane. The Origin of General Absorption.*

By THOMAS MARTIN LOWRY and ROSE RACHEL SASS.

1. *Purpose of the Experiments.*

(*a*) THE observations described in the preceding paper created the impression that, just as the selective absorption of the ketones can be attributed to some form of polar activation or incipient ionisation of the *double* bond of the carbonyl group, so their general absorption might be attributed to the activation or incipient ionisation of a *single* bond, *e.g.*, between carbon and hydrogen or between carbon and a halogen. In camphor itself, the single bonds appear to be so strong that they can only be activated by, and can therefore only absorb, light of very high frequency; the corresponding maximum of "general" absorption is therefore so remote that even the foot of the band cannot be detected at a wave-length of 2400 Å.U. On the other hand, in αα′-dibromocamphor (where the bonds between carbon and bromine are so weak that the compound acts as an oxidising agent) the general absorption is so strong that it almost covers up the selective absorption. The increase of absorptive power is indeed so rapid as to indicate that it must reach a maximum at a wave-length not far beyond the limits of our experiments. We therefore formed the opinion that, just as the double bond of the carbonyl group produces a characteristic absorption at about 2700 Å.U., so the single bond between carbon and bromine might have a characteristic absorption at some shorter wave-length; and that just as the maximum of the ketonic band of camphor can be shifted to the extent of some 350 Å.U. under the influence of contigu-

ous negative atoms, so the band of general absorption might be shifted through some hundreds of Ångström units in the direction of longer wave-lengths, as a result of the weakening of the single bond under the influence of contiguous negative atoms. This view, which served to explain the close analogy between the influence of the halogens on the selective and on the general absorption of the halogen derivatives of camphor, had the advantage that it could be tested by direct experiments on a much simpler series of compounds, and in this way it led to the experiments on the general and selective absorption of the halogen derivatives of methane, which form the subject of the present paper.

(*b*) In the experiments on general absorption advantage was taken of the fact that the introduction, first of the sector-photometer and then of the ultra-violet spectrophotometer, has made it possible to measure the molecular extinction coefficients of a solution in the ultra-violet region, and so to make an exact quantitative comparison of the general absorptions of a series of substances. Previous observations, in which the older qualitative methods were used (Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1183; Massol and Faucon, *Compt. rend.*, 1917, **164**, 813), had given numerical values only for the characteristic wave-lengths of the iodo-compounds, which are the only ones to show a selective absorption in the accessible ultra-violet region.

(*c*) On the supposition that a marked general absorption could be produced by the incipient ionisation of a weak single bond between carbon and a halogen we anticipated :

(i) That the general absorption would increase progressively in the series CH_3F, CH_3Cl, CH_3Br, CH_3I, since the bond between carbon and fluorine is known to be extremely strong, whilst the bond between carbon and iodine is so weak that it can be ionised quite readily, *e.g.*, in the formation of a methiodide from an alkyl iodide and a nitrogenous base, or in the interaction between methyl iodide and silver nitrate in the Zeisel method of estimating methoxyl groups.

(ii) That the general absorption would increase in series such as :

$$\begin{array}{llll} CH_3Cl, & CH_2Cl_2. & CHCl_3, & CCl_4, \\ CH_3Br, & CH_2Br_2, & CHBr_3, & CBr_4, \quad \text{or} \\ CH_3I, & CH_2I_2, & CHI_3, & \end{array}$$

since the accumulation of negative atoms would tend to weaken the bond between the carbon and the halogen, and so bring the crest of the band nearer to the accessible ultra-violet region. These anticipations have been fulfilled, as can be seen from the following summary of the experimental results.

2. *Summary of Experimental Results.*

The experimental data in reference to the halogen derivatives of methane are shown in Fig. 1, and are summarised in Table I.

TABLE I.

Absorption Spectra of Alcoholic Solutions of Halogen Derivatives of Methane.

Formula of substance.	Wave-lengths for integral values of log ϵ. log ϵ = 0·0.	1·0.	2·0.	3·0.	4·0.
$CHCl_3$	2320				
CCl_4	2700	2500	2360		
CH_3Br	2640	2360			
CH_2Br_2	2900	2700	2560	2300	
$CHBr_3$	—	3000	2900	2400	
CBr_4	—	3600	3300	2600	
CH_3I	—	3000	2900		
CH_2I_2	3900	3720	3600	3200	
CHI_3	—	—	4500	3900	2200

Position of maxima.

	(*a*) Lowry and Sass. Å.U.	(*b*) Crymble, Stewart, and Wright.				(*c*) Massol and Faucon.			
I_2	log ϵ = 2·7 at 4770 log ϵ = 3·3 at 2900	4800	—	3030	—	4700	3500	2880	—
CH_3I	log ϵ = 2·7 at 2600	—	—	—	2570	—	—	—	2500
CH_2I_2	log ϵ = 3·1 at 2960	—	—	3030	—	—	—	2880	—
CHI_3	log ϵ = 3·5 at 3450, 2940	—	3570	3030	—	—	3350	2880	—
CI_4						—	3450	2880	—
KI_3	log ϵ = 3·9 at 3550, 2900	—	3570	3030	—				

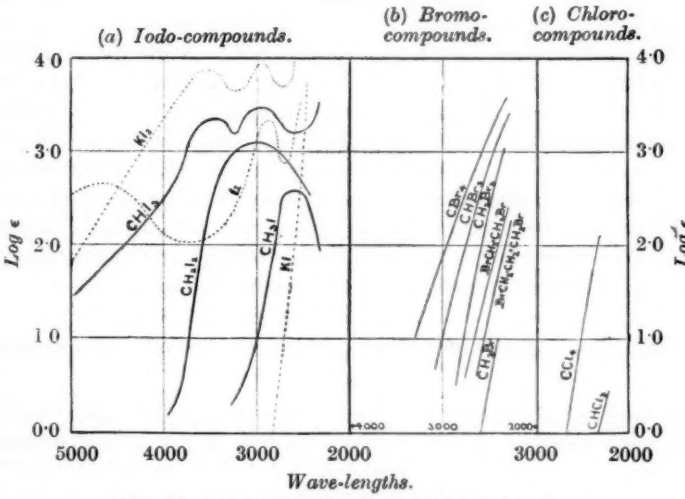
(i) The data recorded above show that the absorptive power of the chlorine compounds is very slight. Thus even chloroform only produces a measurable absorption at high concentrations and short wave-lengths, *e.g.*, the value of log ϵ at 2400 Å.U. is only −1·0. Carbon tetrachloride, however, develops a marked absorptive power at 2700 Å.U., where log ϵ = 0·0, and gives rise to a well-defined curve of general absorption (Fig. 1, *c*).

(ii) Just as $\alpha\alpha'$-dibromocamphor gives rise to a much greater general absorption than $\alpha\alpha'$-dichlorocamphor, so the bromo-derivatives of methane are much more absorptive than the corresponding chloro-compounds. Thus methyl bromide is nearly as absorptive as carbon tetrachloride; and the general absorption becomes increasingly strong in the series CH_3Br, CH_2Br_2, $CHBr_3$, CBr_4 (Fig. 1, *b*), until in the last compound the foot of the band begins to approach the violet end of the visible spectrum. It is noteworthy that the general absorption of β-bromocamphor, where the distance between the bromine atom and the oxygen of the ketonic group is sufficiently great to prevent the two negative radicals from influencing each other to any large extent, is very similar to that of methyl

bromide; thus the molecular extinction coefficient, which rises to $\log \varepsilon = 1{\cdot}1$ at 2500 Å.U. in β-bromocamphor, reaches the same value at 2400 Å.U. in methyl bromide. This result is in harmony with the view that in both cases the weak bond which gives rise to the general absorption is the bond between carbon and bromine.

(iii) Conclusive evidence that the general absorption of the halogen derivatives of methane is due to a band of short wave-length, and that this wave-length can be increased by weakening the bond which links the halogen to the carbon, was obtained from the study of the iodides of the series CH_3I, CH_2I_2, CHI_3. In this series, although we only expected to find an enhanced "general absorption,"

FIG. 1.



Absorption spectre of halogen derivatives of methane.

definite bands are in fact developed (Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1183; Massol and Faucon, *Compt. rend.*, 1917, **164**, 813). Up to a certain point the extinction coefficients of methyl iodide are almost identical with those of bromoform, *viz.*, $\log \varepsilon = 1{\cdot}0$ at 3000 Å.U. and 2·0 at 2800 Å.U.; but the curve for the iodide, instead of rising progressively to $\log \varepsilon = 3{\cdot}0$ at 2400 Å.U., reaches a maximum, $\log \varepsilon = 2{\cdot}6$ at 2600 Å.U., and then falls again to $\log \varepsilon = 2{\cdot}0$ at 2327 Å.U. (Fig. 1, *a*).

(iv) The absorption band, which thus makes its appearance for the first time in methyl iodide, develops progressively in the series CH_3I, CH_2I_2, CHI_3, until, in the case of iodoform, the foot of the band extends half-way across the visible spectrum. The visible colour of this compound, however, unlike that of *p*-benzo-

quinone, is still due to a selective absorption in the ultra-violet. The appearance of a general absorption beyond the band is a novel feature, which was seen for the first time in iodoform; but no great significance appears to attach to it, since it merely suggests the existence of a reserve of bands of shorter wave-length, which can be shifted towards the accessible ultra violet region by the accumulation of negative atoms.

(v) The most interesting feature of the iodoform curve is the division of the crest of the band into two maxima, $\log \varepsilon = 3{\cdot}5$ at 3450 and 2940 Å.U., separated by a shallow minimum. It is not certain, however, whether even this should be regarded as an entirely abrupt development, since the band becomes progressively wider on passing from methyl iodide to methylene iodide and then to iodoform, although a careful examination failed to reveal any similar subdivision of the crest of the band in methylene iodide. The general form and position of the curves certainly suggest that we are dealing with the same band throughout, and that, although the second and third atoms of iodine may reinforce and develop the band, they are not needed in order to initiate it. It is, however, equally clear that the striking development of the band in methylene iodide and in iodoform reveals the influence of certain novel factors, which are not present in the simple alkyl iodides and are sufficiently important to form the subject of a separate discussion.

3. *Absorption Spectra of Iodine, Potassium Iodide, and Potassium Tri-iodide.*

In view of the qualitative comparisons which earlier workers have made between the absorption spectra of the iodo-derivatives of methane and those of solutions of iodine in alcohol and in aqueous potassium iodide, we have thought it desirable to include these solutions in our series of quantitative measurements. The results are shown in Fig. 1, *a*, together with a curve of general absorption of potassium iodide. They have also been included in Table 1. The general conclusions are as follows:

(*a*) Although visible colour is developed more readily in compounds of iodine than in those of the other halogens, so many colourless compounds of iodine are known that one must suppose its chromophoric properties to be like those of oxygen, which depend on the mode of combination of the element, rather than like those of chromium or cobalt, where the elements seem to be almost incapable of yielding colourless derivatives. It is, therefore, very doubtful whether Massol and Faucon were justified, after recording the existence of three bands at 4700, 3500, and 2880 Å.U. in an alcoholic solution of iodine, in identifying these same bands in the

absorption spectra of the iodo-derivatives of methane. A theoretical objection to this method of treatment is found in the fact that, according to the conventional view, the atoms of iodine in an alcoholic solution are linked only by iodine–iodine bonds, whilst in the iodo-derivatives of methane all the atoms of iodine are held by carbon–iodine bonds. There is, therefore, no obvious basis for an identity of characteristic frequency, unless it arises from the inherent properties of the iodine atom or molecule; and the former alternative at least is ruled out by the fact that the frequency of the band in methyl iodide (2600 Å.U.) is so far different from that of the iodine bands that Massol and Faucon did not attempt any identification in this case. On the experimental side, this identification is limited by the fact that the band at 4800 Å.U., which imparts a visible colour to the alcoholic solution of iodine, is not reproduced in any of the derivatives, the colour of which is invariably due to the extension into the visible spectrum of the foot of an ultra-violet band. The second band at 3500 Å.U. can also be omitted from the discussion, since it is not recorded by Crymble, Stewart, and Wright, and no trace of it can be found on the quantitative curves which we have plotted in Fig. 1, *a*. It is therefore only the third band, at 2900 Å.U., that is available for the purpose of identification.

A band at 2900 Å.U. occurs in the absorption spectrum of iodine in aqueous potassium iodide, as well as of iodine in alcohol; but it is accompanied by a second band at 3500 Å.U., which is of much shorter wave-length than the visible band at 4770 Å.U. of the alcoholic solution. It is, therefore, impossible to attribute the selective absorption at 2900 Å.U. to the presence of free iodine in the aqueous iodide solution. If, therefore, the band is really the same in the two cases, it must be ascribed to some identical type of bond between the atoms of iodine, a conclusion against which no theoretical objection can be urged.

We have already seen that the wave-length of the band in methyl iodide is less than in elementary iodine; but in methylene iodide it is approximately equal to it. Since ethylene iodide gives a band of the same frequency as methyl iodide, although of rather greater intensity, Crymble, Stewart, and Wright attribute the methylene iodide band to the juxtaposition of two atoms of iodine in the same molecule, *i.e.*, they suggest that I–$\overset{\displaystyle I}{\underset{\displaystyle I}{C}}$–I gives the same band as I–I, but that I–$\overset{\displaystyle I}{\underset{\displaystyle I}{C}}$–$\overset{\displaystyle I}{\underset{\displaystyle I}{C}}$–I behaves like –$\overset{\displaystyle I}{\underset{\displaystyle I}{C}}$–I. Our own measurements indicate, however, that the band in methylene iodide reaches a maximum at 2960 Å.U., and is definitely of lower frequency than the iodine band at 2900 Å.U. It is, moreover, quite different in appearance, and could only be identified with the iodine band on the

assumption that it was really a double band, of which one component was identical with one of the bands of elementary iodine. It is therefore only in iodoform that any real identification is possible.*

(*b*) Whilst Massol and Faucon attempt (perhaps somewhat unreasonably) to identify the bands of elementary iodine with those of its derivatives, Crymble, Stewart, and Wright associate together the spectra of potassium tri-iodide and iodoform. This identification appeared at first sight to be at least equally unreasonable, since the colour of the tri-iodide is always attributed to the negative ion I_3^-, which (like iodine itself) can only contain iodine–iodine bonds, whilst in iodoform the three atoms of iodine have always been regarded as linked independently to a central atom of carbon. Before accepting so remote an identification, therefore, we regarded it as essential to plot quantitative absorption curves for the two substances. The result has been to establish a degree of resemblance which is even closer than that shown by the qualitative curves. Thus (i) each spectrum includes two bands, and only two, in the accessible range of the spectrum.

(ii) The foot of the band of longer wave-length extends in each case into the visible spectrum and gives rise to visible colour.

(iii) In the same way, the band of shorter wave-length is followed almost immediately by a strong general absorption.

(iv) The persistence of the band of shorter wave-length is thereby limited to about 0·25 in both compounds.

(v) The two crests are of similar wave-length, namely, 3500 and 2900 Å.U. for potassium tri-iodide and 3450 and 2940 for iodoform.

(vi) In both cases the two crests are of equal intensity.

(vii) They are also separated by a shallow minimum which limits the persistence of the band of longer wave-length to about 0·25 in both cases.

(viii) Finally, the intensities of the bands on the absolute scale, although not identical, are almost the same in the two cases, namely $\log \varepsilon = 3{\cdot}5$ for iodoform and 3·9 for potassium tri-iodide.

These eight points of agreement, which appear to us to be far beyond the possibilities of a mere coincidence, point to the existence of some definite similarity of structure between the two compounds. No such similarity is indicated, however, by any of the conventional formulæ. Thus, the most plausible formula for the I_3^- ion is perhaps

* Carbon tetraiodide is so unstable in alcoholic solution that it was not investigated by Crymble, Stewart, and Wright, nor by ourselves; we cannot therefore say what weight should be attached to the statement of Massol and Faucon that it gives the same bands as iodoform.

one which represents it as the analogue of the HF_2^- ion, *e.g.*, $\overset{+}{K}[\overset{-}{I}\overset{+}{I}\overset{-}{I}]$ (compare $\overset{+}{K}[\overset{-}{F}\overset{+}{H}\overset{-}{F}]$); but the formula of iodoform cannot be made to conform to this pattern, since it has always been assumed that the three atoms of iodine are linked directly to carbon and not to one another. The stricter rules of the electronic theory of valency forbid, in an even more emphatic manner than before, any tampering with these formulæ, *e.g.*, by assigning a higher covalency to iodine, and thus superposing a ring structure on the traditional tetrahedron. We can therefore only conclude that our present theories of valency are inadequate to express certain features of molecular structure which may become of predominant importance in cases such as that now under consideration. It appears, indeed, as if both molecules were dominated by a cluster or ring of three contiguous iodine atoms, just as (according to W. L. Bragg's recent determinations) the crystal structure of most of the oxy-salts and of many of the metallic oxides is dominated by clusters of contiguous oxygen atoms, leaving the co-ordinating atom to occupy a mere cavity between the oxygens. This picture, from which all traces of the bonds between the atoms have been erased, is admittedly unconventional, but it appears to be the only one which gives any clue to the origin of the amazing similarity of the two absorption spectra.

4. *Summary and Conclusions.*

(*a*) The general absorption of the chloro- and bromo-derivatives of methane increases progressively from chloroform to carbon tetrabromide. Methyl iodide, however, produces a band which becomes more intense and of longer wave-length on passing to methylene iodide and to iodoform, where the crest of the band is finally resolved into two maxima.

(*b*) The ultra-violet absorption band of methyl iodide cannot be explained by any of the older theories of colour, but finds a simple explanation in the relative weakness of the bond between carbon and iodine, and the consequent smallness of the quanta of energy that are required to activate it. The suggestion is therefore made that the general absorption of the halogen derivatives of camphor and of methane, and the intensification of the general absorption by an accumulation of contiguous negative atoms, is due to the activation or incipient ionisation of a single bond, just as the ketonic band of camphor may be attributed to the activation or incipient ionisation of the double bond of the carbonyl group.

(*c*) There is a close resemblance between the absorption spectra of iodoform and of potassium tri-iodide, which is not accounted for by the formulæ commonly assigned to these compounds, and appears

to be beyond the scope of our present theories of valency. It may, however, be due to the presence of three contiguous atoms of iodine in the space models of the two compounds.

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CAMBRIDGE. [*Received, November 19th*, 1925.]

LXXXV.—*The Equivalent Conductivity of Solutions of Sodium Hydroxide and the Mobility of the Hydroxyl Ion.*

By HUMPHREY RIVAZ RAIKES, ALBERT FREDERICK YORKE, and FREDERICK KENNETH EWART.

THE object of the work detailed in this paper was to make use of the very pure water obtainable from stills of the type described by Bourdillon (J., 1913, **103**, 791) for determining the value of the mobility of the hydroxyl ion.

It has long been recognised that the chief impurity in conductivity water is carbon dioxide. Present as it is in extremely small quantities, its effect on the conductivity of solutions of salts and to a less degree of acids may well be regarded as negligible and the true value of the conductivity is obtained from the observed value by subtracting a "water-correction."

With hydroxides, however, the case is quite different, since slow-moving carbonate ions are substituted for mobile hydroxyl ions and in very dilute solution the conductivity is that of a carbonate and not that of a hydroxide. The observed values will thus be less than the true values and if anything a correction should be added instead of subtracted.* As, however, the determination of the value of this correction is not a simple matter, our method has been to use only water of the highest purity and to regard the whole conductivity as being due to the hydroxide.

The still used was a slightly modified Bourdillon still. It delivered, in quantity, water of specific conductivity 0·06—0·07 gemmho, and in the best experiments this had not increased beyond 0·09 gemmho after the water had been transferred to the conductivity cell.

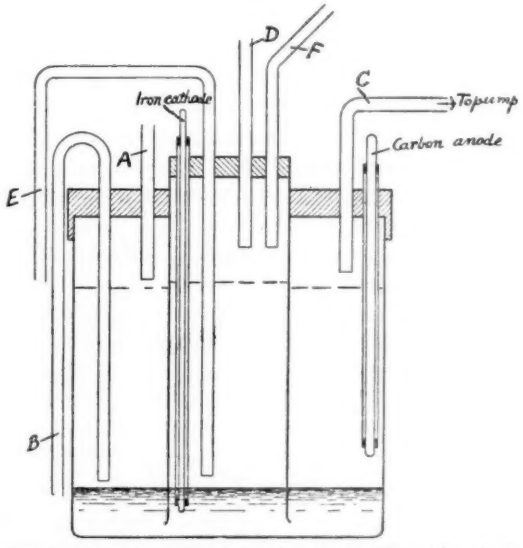
* Mr. W. F. K. Wynne-Jones has very kindly examined our figures and in one run where water of 0·599 gemmho purity was used and in which the equivalent conductivity showed a maximum at a concentration of 0·0007 mol. per litre he has shown that the application of a correction based on the assumption that the conductivity of the water was due to carbon dioxide brings the values obtained into close agreement with those found by us in water of a high degree of purity.

Experimental.

Preparation of Sodium Hydroxide Solutions.—The chief methods available for the preparation of pure aqueous sodium hydroxide are (i) the action of water on metallic sodium; (ii) methods involving the precipitation of the carbonate present in ordinary sodium hydroxide by means of a barium or calcium salt; (iii) the electrolysis of an aqueous solution of a sodium salt.

In the first method, the difficulty is to get rid of the scale of carbonate on the surface of the metal before submitting it to the action of water.

Fig. 1.



Apparatus for the preparation of sodium hydroxide solutions.

In the second method, it is impossible to avoid the presence in the final product of either barium or calcium. Noyes states (*Pub. Carnegie Inst.*, 1907, No. 63) that his final product contained at least 0·1% of barium sulphate.

A very pure product may be obtained, however, by the third method.

A method somewhat similar to ours for obtaining aqueous sodium hydroxide free from carbonate has been described by Jorissen and Filippo (*Chem. Weekblad*, 1909, **6**, 145).

Description of Apparatus.—The cell (Fig. 1) consisted of an outer vessel of common glass about a litre in capacity, carrying a wide glass tube of about 200 c.c. capacity which was made the cathode

compartment. The tube was at first of Jena glass and later of Pyrex glass; no difference in the purity of the final product could be detected. All the glass tubing used was boro-silicate and was well steamed before being made up. The bottom of the cell was covered to the depth of about an inch with mercury, previously distilled in a vacuum.

A tightly fitting wooden cap in the outer vessel carried the cathode compartment and other accessories. The lower end of the cathode compartment dipped well below the surface of the mercury, but did not touch the bottom of the outer vessel. A tightly fitting cork in the top of the cathode compartment itself carried the accessories necessary in this compartment.

The anode consisted of a carbon rod, which was rather rapidly attacked by chlorine; it was protected as far as possible by means of a glass tube, and arranged so that its end was about 1 inch above the mercury surface.

The cathode was of iron protected by a sheath of borosilicate glass tubing; its lower end dipped into the mercury and the iron never came into contact with the solution in the cathode compartment.

At first the whole apparatus was arranged so that it could be rocked gently in order to facilitate the passage of the sodium amalgam into the cathode compartment. This rocking was, however, found to be unnecessary and was abandoned.

The current used was about 2·3 amps. when the cell could be watched, but when it had to be left this was reduced to 1·2 amps. in order to avoid the risk of heating.

Procedure when Working the Cell.—The mercury having been run into the cell, the cap was placed in position and sealed on. As an additional precaution, the whole of the outside of the cap was covered with a layer of high melting-point paraffin-wax.

The cathode compartment was washed from five to six times with fairly good conductivity water; the water being run in through *D* and syphoned out through *E*.

A normal solution of sodium chloride (Merck) made up with water of about 0·5 gemmho conductivity was run into the anode compartment through the tube *A*, so that the level of the liquid was about an inch below the end of *C*; the tube *A* was then fitted with a soda-lime tube.

A current of dry air, free from carbon dioxide and ammonia, was next passed through the cathode compartment, *via* the tube *F*, the tubes *D* and *E* during this operation carrying soda-lime tubes; after this, the tube *F* was connected to a soda-lime tube.

Finally, about 200 c.c. of pure water (0·3 gemmho conductivity)

were run into the cathode compartment through the tube *D*, which was connected to the flask delivering the water, so that at no time did the latter come into contact with the atmosphere. The tubes *D* and *E* were then closed.

The current was now switched on, the hydrogen evolved at the cathode escaping through the soda-lime tube connected with *F*, and the chlorine being drawn off through *C* by means of a water pump; it was found necessary to connect the tube *A* to the air (through a soda-lime tube) in order to prevent a reduction of pressure taking place in the anode chamber, and consequent passage of the cathode liquid into the anode compartment. The exhausted brine was syphoned off through *B*.

Care was taken to keep the temperature of the cell as low as possible during the reaction, in order to prevent the solution of silica. The temperature at no time rose above 40° and was usually kept between 25° and 30°.

After the current had passed for about 6 hours, some of the sodium hydroxide in the cathode compartment was drawn off, and its strength roughly estimated. The solutions eventually used varied from $N/10$ to N. The main quantity of solution was then transferred by suction to a Jena glass flask which had been previously steamed and filled with pure air.

Thus the sodium hydroxide solution never came into contact with the air of the room at any time during its preparation. The solution was stored in this flask until required for a dilution, but was rarely kept for more than 3 days before being so used.

Purity and Analysis of the Sodium Hydroxide Solutions.—The sodium hydroxide prepared as above was invariably tested for chlorine and carbon dioxide, the former by the nephelometric method of Richards (*Amer. Chem. J.*, 1904, **31**, 235; 1906, **35**, 99), and the latter by mixing with baryta in the nephelometer by a method which enabled the solutions to be compared without any risk of contamination by carbon dioxide. The solutions never showed a greater cloudiness than a clear solution of baryta which was used as standard. Chlorine was always absent. The analysis of the solutions was carried out by means of weight titrations against hydrochloric acid, with methyl-red as indicator. The analyses were always done in triplicate and never differed by more than 1 part in 10,000. The hydrochloric acid was purified and estimated by Richards's method (*J. Amer. Chem. Soc.*, 1905, **27**, 459). Three analyses of each sample were made and the results agreed to 1 part in 20,000.

The weights used were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144) and the appropriate vacuum correction was always applied. The densities of the sodium

hydroxide and hydrochloric acid solutions were taken from Landolt and Bornstein's tables.

The Conductivity Measurements.—The cell used was one designed by Hartley and Barrett and will be described in a future publication. It consisted essentially of a 1500 c.c. Jena glass beaker, to the top of which was cemented a brass ring. To this ring was attached by means of screws a silver-plated brass cover which carried the electrodes, a stirrer, and a thermometer, and was provided with two openings through one of which a stream of pure air could be passed, whilst the tip of the weight pipette was inserted through the other. These openings could be closed at will. The electrodes were coated with platinum black.

All the resistances were calibrated against Wolff standards which had been recently restandardised at the National Physical Laboratory.

The cell constant, determined in the manner described by Frazer and Hartley (*Proc. Roy. Soc.*, 1925, *A*, **109**, 355), had the value 0·1367, identical with the value obtained by Hartley and Barrett in 1909.

The Thermostat.—The temperature variation of the bath was never more than $\pm 0{\cdot}01°$ and for most of the runs it did not exceed $\pm 0{\cdot}005°$.

The Weight Pipette.—The weight pipette used for adding the solution to the cell was provided with a filling arrangement which effectually prevented the contamination of the solution by the carbon dioxide of the air.

A run was carried out by adding weighed portions of stock solution to the solvent in the cell.

Cleaning and Drying the Cell.—After each run the cell was rinsed out several times with pure water, and the electrodes, thermometer, and stirrer were cleaned by means of a stream of water. The cell was then filled with about a litre of pure water, the top placed in position, and the stirrer set going for several hours. The water was changed at least once a day and stirred. When the cell was required for a run, the beaker was inverted and allowed to drain for about 6 hours; the rest of the cell was also drained. For the first two runs the beaker was finally dried by means of filter-paper; the thermometer and stirrer were dried in a similar manner. The electrodes were dried by just touching their edges with filter-paper.

It was found later that the water was of better quality if the beaker was not wiped, but if, after draining, the top was placed in position and a current of dry air passed through it for several hours, the stirrer being rotated in order to keep the air circulating. This was found to be a very effective method of drying.

The Results.—In all, seven runs were carried out at 18° and two at 10°. The figures in Tables I and II show that even in the best water the equivalent conductivity fell off in solutions less concentrated than $N/1000$. In some of the earlier runs the values obtained were quite untrustworthy.

All concentrations are given in gram-molecules per litre at the temperature of experiment (NaOH = 40).

TABLE I.

Equivalent Conductivity of Sodium Hydroxide at 18°.

Uncorrected for solvent conductivity.

Run H. 31/5/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·086 gemmho.

Conc. × 10^4	0·266	0·576	0·889	2·45	7·24	17·87	29·9
Λ	171·8	185·0	189·0	200·7	205·0	208·0	208·0

Run K. 12/6/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·084 gemmho.

Conc. × 10^4	2·54	5·85	11·28	22·5	48·7	99·5	170	319
Λ	208·3	211·4	214·4	213·6	211·4	209·5	207·6	203·8

Run L. 20/6/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·087 gemmho.

Conc. × 10^4	10·5	22·3	41·2	76·4	158	277	545
Λ	215·0	213·7	212·0	210·1	207·9	204·9	198·1

TABLE II.

Equivalent Conductivity of Sodium Hydroxide at 10°.

Uncorrected for solvent conductivity.

Run D. 29/4/1922. $T = 10° \pm 0{\cdot}01°$. Water 0·082 gemmho.

Conc. × 10^4 ...	0·431	1·26	8·42	17·6	33·1
Λ	152·4	169·1	178·3	178·6	178·0

Run M. 22/6/1922. $T = 10° \pm 0{\cdot}01°$. Water 0·089 gemmho.

Conc. × 10^4 ...	9·74	18·9	36·7	73·5	144	285
Λ	179·2	178·2	177·0	176·6	175·1	173·0

Fig. 2 gives the graph of equivalent conductivity plotted against the square root of the concentration, and it will be seen that for solutions more concentrated than $N/1000$ the points lie on straight lines up to a concentration of $N/30$. The equations to these lines are :

$$\text{at } 18°,\ \Lambda_{18} = 217 - 75{\cdot}7\sqrt{c}$$
$$\text{and at } 10°,\ \Lambda_{10} = 180{\cdot}2 - 44{\cdot}2\sqrt{c},$$

c being the concentration of the solution in gram-molecules per litre at the temperature of experiment.

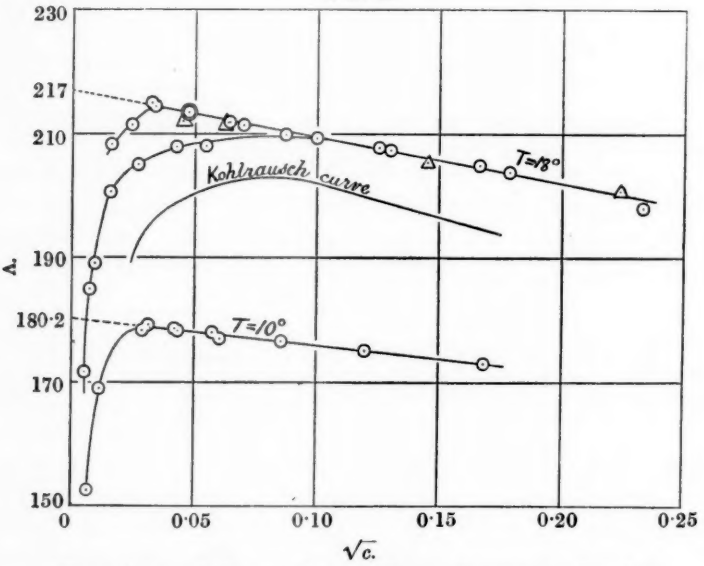
Noyes (*loc. cit.*), whose sodium hydroxide was estimated by himself to contain 0·1% of barium sulphate, gives four values for the equivalent conductivity which lie about 0·5% below our values (see Fig. 2).

For comparison, the values obtained by Kohlrausch (*Wied. Ann.*, 1885, **26**, 197) are also plotted in Fig. 2.

The Temperature Coefficient of Equivalent Conductivity between 10° *and* 18°.—The temperature coefficient calculated from the above figures is 4·60. The value obtained by Noyes (*loc. cit.*) for the range 18—100° was also 4·60.

The Mobility of the Hydroxyl Ion.—The mobility of the sodium ion at 18° being taken as 43·4 (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 479), the mobility of the hydroxyl ion becomes 173·6 at 18°.

FIG. 2.



The points marked △ are those of Noyes; the concentrations have been recalculated to gram-mols. per litre.

If the mobility of the sodium ion as calculated by Washburn (*J. Amer. Chem. Soc.*, 1918, **40**, 158) is taken to be 43·23, the value for the hydroxyl ion becomes 173·8.

On the somewhat untrustworthy assumption that the transport number of the hydroxyl ion in sodium hydroxide has the same value at 18° and 10°, the mobility of the hydroxyl ion at 10° is, using the Noyes and Falk value for the sodium ion, 144·2, and using the Washburn value, 144·3.

Summary.

The equivalent conductivity of solutions of sodium hydroxide has been measured at 18° and 10° and the values for infinite dilution found to be 217·0 and 180·2, respectively.

Using Washburn's value for the mobility of the sodium ion, the mobility of the hydroxyl ion is found to be 173·8 and 144·3 at the two temperatures.

The authors wish to express their indebtedness to the Research Fund Committee of the Chemical Society for assistance in purchasing a part of the apparatus used for the still, to the authorities of Balliol and Trinity Colleges for permission to use their laboratory, and in particular to Brigadier-General H. Hartley for his continued interest and advice during the course of the work.

EXETER COLLEGE, OXFORD. [*Received, November* 21*st*, 1925.]

LXXXVI.—*The Mercuration of Aromatic Substances. Part II.* o-*Nitrotoluene.*

By SAMUEL COFFEY.

THE position taken up by the acetoxymercuri-group in the mercuration of benzenoid compounds is sometimes anomalous; thus in the mercuration of nitrobenzene 50 and 40% of the *o*- and *m*-compounds respectively are formed, whilst with toluene the proportions of the three isomerides are $o:m:p = 43:13:44$ (J., 1925, **127**, 1029).

In the mercuration of the three mononitrotoluenes, which has now been studied, the reaction does not follow the expected course. This paper deals with the results obtained on mercurating *o*-nitrotoluene. When a third substituent is introduced into this compound, the 1 : 2 : 6 and 1 : 2 : 4-derivatives are generally the chief products. Of the four possible chloromercuri-*o*-nitrotoluenes, the 1 : 2 : 4-compound was isolated in quantity, the 1 : 2 : 6-compound was proved to be present in relatively large amounts, and the formation of the 1 : 2 : 3- or 1 : 2 : 5-derivative also was demonstrated. Attempts that were being made to discover which of these two was actually present were abandoned when the author was informed that Dr. Kenner, working at Sheffield, had obtained the 1 : 2 : 3-derivative in considerable quantity by mercurating *o*-nitrotoluene.

Although nitrotoluenes react with mercuric oxide and hot caustic soda solution to give compounds containing mercury in the side chain (Reissert, *Ber.*, 1907, **40**, 4209), no mercurinitrotoluenes containing mercury directly attached to the nucleus are known. These are readily obtained when *o*-nitrotoluene is heated with mercuric acetate at 140°.

For comparison and in order to see whether the 1 : 2 : 3- and

1 : 2 : 5-derivatives differed at all in physical properties from the normal substitution products, 4-chloromercuri- and 5-chloromercuri-2-nitrotoluene were made synthetically through the corresponding sulphinic acids (compare Peters, *Ber.*, 1905, **38**, 2567).

Experimental.

Mercuration of o-*Nitrotoluene.*—From the product of reaction in boiling acetic acid, only mercurous acetate and the internal anhydride of monohydroxymercuri-acetic acid were isolated.

The mercuration was best carried out as follows: Mercuric acetate (1 part) and *o*-nitrotoluene (4 parts) were heated gradually with occasional shaking. At 110—120°, the mercuric salt became orange-red and viscous, the solution frothed slightly, and acetic acid distilled off. As the temperature increased, the red mass gradually disappeared and a pale yellow solution formed. A temperature of 140—150° was attained after an hour's heating and was maintained until the product failed to respond to a test for mercuric ions (4 hours). After 12 hours, a brown, amorphous solid, containing a little free mercury but consisting mainly of mercurous acetate, separated.

The clear nitrotoluene solution was then poured into a large volume of ether and left for 24 hours, when an almost colourless, amorphous solid separated. This had a high mercury content and apparently consisted of polymercuri-compounds; it was free from monoacetoxymercuri-derivatives. The ether was distilled off, the clear yellow solution treated with an excess of sodium chloride solution to convert the acetoxymercuri-compounds into the more easily purified chloro-derivatives, and the excess of nitrotoluene removed as quickly as possible in a current of steam. The main product of the reaction remained as a heavy, almost colourless mass. This was broken up and allowed to dry in the air. The yields (in grams) of the various products obtained in different experiments were:

	I.	II.	III.	IV.
Nitrotoluene used	210	310	1000	360
Mercuric acetate	50	75	200	90
Insoluble in nitrotoluene	3	7½	18	5
Insoluble in ether	9	15½	35	15
Main product	40	55	166	69

This crude main product contained a small amount of nitrotoluene which was retained very tenaciously but was finally removed by extraction with ether in a Soxhlet apparatus. The residue melted at 120—155° and consisted only of monochloromercuri-*o*-nitrotoluenes (Found: N, 3·75. $C_7H_6O_2NClHg$ requires N, 3·8%).

Separation and Orientation of 4-*Chloromercuri*-2-*nitrotoluene.*—By crystallising the crude product (160 g.) twice from 500 c.c. of hot

acetone the pure compound was obtained in silky needles, m. p. 220·5—221° (corr.), having, when dry, the appearance of asbestos. By working up the mother-liquors a total yield of 32 g. was obtained (Found: N, 3·7; Hg, 53·9. Calc., N, 3·8; Hg, 53·9%).

4-Chloromercuri-2-nitrotoluene is sparingly soluble in all usual solvents except acetone and hot glacial acetic acid. By treatment with the theoretical quantity of bromine in chloroform it was slowly but quantitatively converted into 4-bromo-2-nitrotoluene, which crystallised from methyl alcohol in slender needles, m. p. 44·5—45°; when it was crystallised very slowly it was obtained in large, pale yellow, brittle prisms (compare Hübner and Roos, *Ber.*, 1873, **6**, 799).

Most organic mercury compounds react with iodine very readily, but the reaction of 4-chloromercuri-2-nitrotoluene with an equivalent of iodine in chloroform required 11 or 12 days for completion, theoretical yields being obtained of mercuric chloride, mercuric iodide, and 4-iodo-2-nitrotoluene, which crystallised from methyl alcohol in small, brittle prisms, m. p. 60·5—61°, identical with that obtained by Heynemann (*Annalen*, 1871, **158**, 345) and Reverdin (*Ber.*, 1897, **30**, 3001).

4-*Bromomercuri*-2-*nitrotoluene* was prepared by treating a solution of the chloro-compound in aqueous acetone with potassium bromide; after boiling for a few minutes, it was cooled, filtered, and the solid washed with water, and recrystallised from acetone. It is a heavy, crystalline powder, m. p. 241° (corr.), less soluble than the chloro-compound.

4-*Iodomercuri*-2-*nitrotoluene*, prepared in a similar manner, melts at 286° with slight decomposition. It was recrystallised from acetone, in which it was only sparingly soluble.

4-*Mercuribis*-2-*nitrotoluene*.—No mercuri-bis-nitro-compounds are known with the exception of mercuribistrinitrobenzene, obtained by heating mercuric trinitrobenzoate. The mercuribisnitrotoluene was obtained by carefully reducing the above chloro-compound with the calculated quantity of sodium sulphide. Under these conditions the chloromercuri-group is attacked before the nitro-group, owing no doubt to the fact that *o*-nitrotolyl mercuric sulphide is first formed and this unstable compound on warming undergoes spontaneous decomposition. In this way, the reducing agent is effectually "fixed" and cannot react with the nitro-group.

4-Chloromercuri-2-nitrotoluene (3·7 g.) was shaken in a solution of crystallised sodium sulphide (1·2 g.) for 3 hours, being thereby converted into the colourless sulphide. The mixture was heated on the water-bath for 2 hours, the black product filtered off, washed, dried, boiled with acetone, and the solution filtered hot. The black,

inky extract, containing colloidal mercuric sulphide, thus obtained was filtered again when cold, the black, colloidal mercuric sulphide passing through the filter and leaving a white, crystalline solid. This spectacular method of purification was repeated until no more solid was obtained. The product was pure *4-mercuribis-2-nitrotoluene*, which crystallises from acetone in a woolly mass of needles, m. p. 291° (corr.) (Found: Hg, 42·0. $C_{14}H_{12}O_4N_2Hg$ requires Hg, 42·4%). On boiling for 3 hours with one equivalent of mercuric chloride in alcohol, it gave an almost theoretical yield of pure 4-chloromercuri-2-nitrotoluene, its constitution being thus determined.

Existence of 6-Chloromercuri-2-nitrotoluene.—The remainder of the mixed chloromercurinitrotoluenes (see p. 638) was suspended in chloroform and treated with bromine (1 mol.), and the bromonitrotoluenes, which were purified by distillation in steam, were obtained in quantitative yield as a golden-yellow oil, freezing at low temperatures to a buttery mass. Attempts to separate this oil into its constituents by means of freezing, fractional distillation in steam, or a vacuum, or by crystallisation, failed. The nitro-compounds were therefore reduced to the corresponding bromotoluidines by warming for 2 hours with sodium sulphide in aqueous alcoholic solution on the water-bath. The amines were distilled in steam, an excess of hydrochloric acid was added to the distillate, and the mixed hydrochlorides were fractionally crystallised; but no pure compound could thus be isolated. The mixture of bases was therefore acetylated, and 7·2 g. of the product were fractionally crystallised as follows. The solution in 50 c.c. of hot 50% acetic acid was filtered, and cooled very rapidly, when 2·1 g. (A) separated, m. p. 150—158°. On standing, the mother-liquor deposited 0·7 g. (B) of pale brown needles, m. p. 159—161°. Only solids with low melting points could be obtained from the final mother-liquor.

On recrystallisation from 10 c.c. of 50% acetic acid (A) gave 1·6 g., m. p. 163—164°, and further recrystallisation from benzene furnished colourless needles of constant m. p. 165·5° (corr.). On hydrolysis this acetyl compound gave a base, m. p. 32°, which was converted into a *benzoyl* derivative, m. p. 160° (corr.). The base was compared with 4-bromo-*o*-toluidine; the latter also melted at 32°, and its acetyl derivative at 165·5—166° (compare Janney, *Annalen*, 1913, **398**, 359), as did also a mixture with (A). The benzoyl compounds were also identical. The yield of 4-bromoaceto-*o*-toluidide isolated was 23%, corresponding to 18% of the original mixed mercurated nitrotoluenes. Hence the total amount of 4-chloromercuri-2-nitrotoluene accounted for is 38%.

The product (B) on recrystallisation from benzene gave 0·55 g.

of long needles, m. p. 162—163°; a mixture with (A) melted at 120—130°. Hydrolysis furnished a liquid base, which was proved to be 6-bromo-*o*-toluidine as follows: 2 : 6-dinitrotoluene was reduced, as described by Noelting (*Ber.*, 1904, **37**, 1018), to 6-nitro-*o*-toluidine. This was diazotised and converted into 6-bromo-*o*-nitrotoluene, m. p. 38°. The latter was reduced to a liquid base, which gave a theoretical yield of the acetyl compound (B) on treatment with acetic anhydride; it melted at 164·5° (corr.).

Some of the melting points of this acetyl compound given in the literature are erroneous; Friedländer, Bruckner, and Deutsch (*Annalen*, 1912, **388**, 30) give it as 163°.

Proof of the Presence of 3- *or* 5-*Chloromercuri*-2-*nitrotoluene.*—Many attempts were made to isolate other derivatives of the bromotoluidines, the bromodinitrotoluenes (obtained by nitrating the mixture of bromonitrotoluenes), or the nitrotoluenesulphonic acids (obtained by sulphonating the original mercuri-compounds), but without success. A small quantity of 3 : 5-dibromo-*o*-toluidine was isolated, which indicated the presence of one or both of the compounds in question, but a more direct proof was obtained by eliminating the amino-group from the mixed bromotoluidines and showing the presence of *m*-bromotoluene in the product.

A mixture of the dry amines, absolute alcohol (4 parts), and 20% oleum (2 parts) was warmed with an excess of sodium nitrite, and the product distilled in steam. The bromotoluenes, which passed over together with a brown substance, were purified by steam distillation from an alkaline solution and repeated fractional distillation, a colourless liquid, b. p. 179—190°, being finally obtained which only partly solidified at — 80°. Hence it was not a mixture of the *o*- and *p*-isomerides only. The mixture was oxidised to the corresponding bromobenzoic acids, and the latter were separated as already described in Part I. In this way pure *m*-bromobenzoic acid, m. p. 154°, was isolated, the presence thus being proved of a substance in the original mixture having the chloromercuri-group in the meta-position with respect to a methyl group and in the ortho- or para-position with respect to a nitro-group; which is abnormal for direct substitution.

Synthesis of 5-*Chloromercuri*-2-*nitrotoluene. Preparation of* 2-*Nitrotolyl* 2-*Nitrotoluene*-5-*sulphazide.*—Almost all the nitrotoluenesulphinic acids are unknown. Since the usual methods of preparation failed here, a process devised by Limpricht (*Ber.*, 1887, **20**, 1238) was used.

Sulphur dioxide was passed into a suspension of 6-nitro-*m*-toluidine (10 g.) in 100 c.c. of alcohol at 0° until absorption ceased. The resulting solution was treated at 0° with nitrous fumes or with

a saturated solution of 20 g. of potassium nitrite with constant stirring. The mixture was kept in ice over-night and at room temperature for 2 days and then poured into water. The bright orange precipitate (9 g.) thus obtained was extracted with boiling alcohol, in which it was only sparingly soluble, and crystallised from glacial acetic acid, 2-*nitrotolyl* 2-*nitrotoluene*-5-*sulphazide* separating in deep orange prisms, m. p. 157—158° (violent decomp.) (Found: N, 15·5. $C_{14}H_{14}O_6N_4S$ requires N, 15·3%).

Fission of a sulphazide by boiling sodium hydroxide solution usually proceeds smoothly: $R{\cdot}SO_2{\cdot}NH{\cdot}NHR' + NaOH = R{\cdot}SO_2Na + R'H + N_2 + H_2O$ (compare Escales, *Ber.*, 1885, **18**, 896). From the nitrotoluene compounds, however, much tar was produced and the acids were difficult to obtain pure by the usual methods. In the preparation of 2-nitrotoluene-5-sulphinic acid and other nitrosulphinic acids good use has been made of the fact that they form insoluble ferric salts, which are unchanged by dilute acids (Thomas, J., 1909, **95**, 342).

The preceding sulphazide was boiled with a slight excess of baryta until no more nitrotoluene escaped with the steam. The deep reddish-brown solution was filtered hot through a wet filter to remove tar, acidified, well diluted, filtered from a little more tar, and treated with an excess of ferric chloride solution. The copious precipitate of ferric salt obtained was boiled with ammonia, the solution filtered from ferric oxide and evaporated to a small volume. On acidification a pale yellow oil separated. This was extracted with ether, and on removal of the solvent, 2-*nitrotoluene*-5-*sulphinic acid* separated in small, colourless needles (Found: equiv., 203. $C_7H_7O_4NS$ requires equiv., 201·1. Found for the ferric salt: Fe, 8·3. $C_{21}H_{18}O_{12}N_3S_3Fe$ requires Fe, 8·3%).

The sulphinic acid was boiled with a 50% aqueous alcoholic solution of mercuric chloride for a week, the solid which separated being filtered off periodically. After washing and drying, the crude chloromercuri-compound was extracted with hot acetone; pure 5-*chloromercuri*-2-*nitrotoluene* crystallised from the solution in a felted mass of small, shining needles, m. p. 210°. In solubility and general properties it was very similar to the 4-isomeride.

2-*Nitrotoluene*-4-*sulphinic Acid*.—When a dilute solution of diazotised 6-nitro-*p*-toluidine was treated with sulphur dioxide and copper powder, a tarry mass was produced immediately. Better results were obtained by working in strongly acid solution, but even then the sulphazide was produced and not the free acid. The base (10 g.) was dissolved in sulphuric acid (75 c.c.) and water (75 c.c.), cooled to 0°, and diazotised; the latter reaction took place very slowly. The solution was saturated at 0° with sulphur

dioxide, and 30 g. of freshly prepared copper powder were added. When the vigorous evolution of gas had ceased, the blue solution was filtered from excess copper and poured into water. The orange precipitate of crude sulphazide (yield 8 g.; no sulphinic acid appeared to be produced) was hydrolysed with hot ammonium hydroxide solution, much tar being produced. The sulphinic acid, which was isolated through the ferric salt as described above, first separated as an oil but was finally obtained as a white, crystalline solid, m. p. 95°. It reacted readily with mercuric chloride in alcoholic solution, giving 4-chloromercuri-2-nitrotoluene identical with that isolated from the mercuration product of *o*-nitrotoluene.

The author wishes to express his thanks to Professor J. N. Collie for the facilities afforded him in his laboratory, and also to the Trustees of the Ramsay Memorial Trust for the grant of a fellowship, during the tenure of which this investigation was carried out.

THE RALPH FORSTER LABORATORIES,
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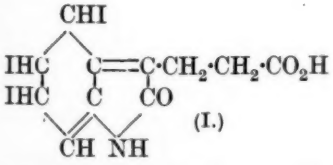
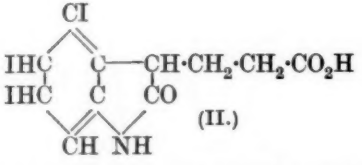
LXXXVII.—*Tautomerism in the Thyroxin Molecule.*

By CEDRIC STANTON HICKS.

IN a previous paper (J., 1925, **127**, 771) a possible relationship between thyroxin and tryptophan was shown, and the evidence pointed to the existence of a benzene nucleus in the substance, which was incompatible with almost complete hydrogenation of the aromatic fragment as postulated by Kendall (*J. Biol. Chem.*, 1919, **40**, 268). He has recently proposed (Chandler Lecture, Univ. Columbia, May, 1925) a modification (II) of his original formula (I), in support of which he offers further experimental proof.



(I.)



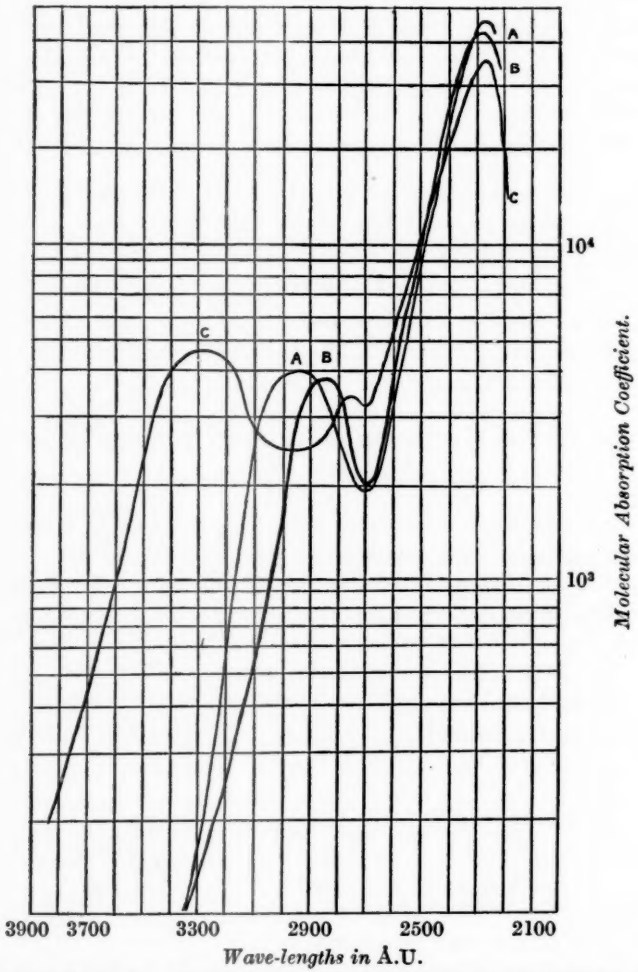
(II.)

A keto-enol type of tautomerism involving the lactim hydrogen is possible, and it was shown in the original work (*loc. cit.*) that the acetyl derivative did not produce the remarkable physiological effect of increase in heat production, when administered to the living organism. Kendall considers this enol transformation to be an intrinsic part of the mechanism whereby the molecule produces the

physiological effect, and further absorption spectrum study was undertaken to investigate this important phase of the subject.

Acetylthyroxin was prepared by Kendall's method (*loc. cit.*) from 20 mg. of commercial thyroxin. It remained amorphous and gummy,

FIG. 1.



A, keto-*Thyroxin*. B, *Acetylthyroxin*. C, *Thyroxin in alkaline solution*.

despite attempts to purify it by crystallisation from alcohol. Through the courtesy of Dr. Kendall, who specially prepared a specimen of the acetyl derivative from pure thyroxin, measurements of the absorption were made possible. The substance was dissolved

in 75% aqueous alcohol and examined in concentrations of $M/2{,}000$, $M/8{,}000$, $M/20{,}000$, $M/50{,}000$, and $M/100{,}000$.

keto-Thyroxin was prepared by dissolving the pure substance in 75% alcohol containing four equivalents of hydrochloric acid, and measurements were made at the same concentrations as the above.

The alcohol-soluble derivative obtained by passing carbon dioxide into a solution containing thyroxin and its equivalent of sodium hydroxide (*loc. cit.*) was dissolved in the minimum of 60% alcohol, and measurements were made as rapidly as possible at concentrations of $M/4{,}000$, $M/20{,}000$, $M/80{,}000$, and $M/100{,}000$.

Discussion.

Allowance must be made for the error in the value of the absorption coefficient likely to arise from the use of such minute quantities of material, but even so the evidence of the wave-lengths of the absorption bands remains. The curves for the acetyl derivative and the keto-form of thyroxin are more closely related to each other than to the curve for thyroxin in alkaline solution. The major band in the last lies at 3275 Å.U., whilst in the other two it lies respectively at 2850 Å.U. and 2925 Å.U., the third band at 2750 Å.U. being absent from both. The curve for the so-called open-ring form, prepared by the action of carbon dioxide on an alkaline solution of thyroxin, is almost identical with that for the *keto*-form, except that it tails off suddenly at 2400 Å.U., in the region of log $\epsilon = 4$, into the Schumann region, giving no band as in the other cases. It is possible that during the time taken to make the measurements, even in dilute alcohol, water may be removed, with consequent closure of the ring, and therefore the results obtained may be intermediate values. The change is represented as follows :

Since the original measurements were made on thyroxin, Friedli has confirmed the presence of the band in indole, in the region 2100 Å.U. (*Bull. Soc. chim. Biol.*, 1924, **6**, 10, 908).

My thanks are due to Professor Sir F. Gowland Hopkins for his continued interest in the work, and to Dr. E. C. Kendall for the gift of acetylthyroxin. This work was done during the tenure of a Beit Memorial Fellowship for Medical Research.

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CAMBRIDGE. [*Received, December 8th*, 1925.]

LXXXVIII.—N-*Alkylated Amidines.*

By MONMOHAN SEN and JÑANENDRA NATH RÂY.

IN connexion with certain investigations relating to glyoxaline alkaloids, it became necessary to prepare and study the behaviour of a number of *N*-alkylated amidines. The methods already available for the preparation of these substances (Wallach, *Ber.*, 1879, **12**, 328; 1882, **15**, 208; 1883, **16**, 357, 1647; Strecker, *Annalen*, 1857, **103**, 328) are not entirely satisfactory. Hofmann (*Jahresber. Fort. Chem.*, 1865, 414; *Monatsberichte Berl. Akad.*, 1865, 640) obtained diphenylacetamidine and diphenylbenzamidine by condensing aniline with acetanilide and benzanilide, respectively, in presence of phosphorus trichloride or pentachloride. This rather convenient method seems to have been little investigated and it was deemed desirable to study it systematically. It is of very general applicability and by its means a number of new amidines have been prepared, in good yield in most cases. Phosphorus trichloride is the most suitable condensing agent for the purpose, although phosphoric oxide in boiling xylene may advantageously replace it in some cases.

A mixture of the requisite quantities of an amine and an acylamine in about ten times the weight of phosphorus trichloride is heated at 110—120° for about 3 hours. The completion of the reaction is indicated by a drop of the reaction mixture giving a clear solution in water. The product is dissolved in cold water and basified; the amidine is then precipitated in a crystalline condition.

The method is applicable to a secondary amine like diphenylamine and an acylamine. On the other hand, acetomethylanilide condenses with *m*-toluidine, hence the reaction is represented as taking place as follows:

$$NH_2R + R'\cdot CO\cdot NHR'' \rightarrow NHR\cdot CR'(OH)\cdot NHR'' \xrightarrow{-H_2O} NR{:}CR'\cdot NHR'' \text{ or } NHR\cdot CR'{:}NR''.$$

But no isomeric forms can be isolated, as the amidines show virtual tautomerism (compare von Pechmann, *Ber.*, 1895, **28**, 869). By altering the order of combination the same product was isolated (A) from acetanilide and *m*-toluidine and from aceto-*m*-toluidine and aniline, and (B) from acetanilide and *p*-nitroaniline and from *p*-nitroacetanilide and aniline. The result (B) is interesting, as here a strongly negative group in the molecule has not impaired the mobility of the hydrogen atom in any way.

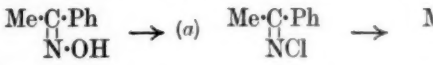
With a view to prepare hydrazidines, we attempted to condense an acylamine with phenylhydrazine by this method. The product

of interaction of acetanilide and phenylhydrazine, on being rendered alkaline, evolved ammonia and diphenylacetamidine was obtained in more than 70% yield.

Next, we attempted to prepare cyclic amidines by using urethane in place of an amine. Phosphoric oxide acting on molar proportions of acetanilide and urethane in boiling xylene solution gave rise to the compound (I), which will be described along with others of the same series in a subsequent communication.

(I.)

A further point of interest is in connexion with the Beckmann transformation of acetophenoneoxime. The transformation may be represented as taking place through the phases (*a*) and (*b*):



Both (*a*) and (*b*) represent reactive chloro-compounds capable of condensing with aniline to form acetophenonephenylhydrazone and diphenylacetamidine respectively. The actual amounts of each would depend on the relative reactivity of the two chlorine atoms in (*a*) and (*b*). Actually, the amidine was produced and no trace of acetophenonephenylhydrazone could be detected. This result may, of course, be due to the smaller reactivity of the chlorine atom in the group C:NCl as compared with N:CCl, but it may also be taken to indicate that the intermediate phase (*a*) exists only for a very short period of time.

EXPERIMENTAL.

Some properties of the amidines that have been prepared are tabulated below. Unless stated otherwise, the amidines were crystallised from alcohol. The values in brackets in column 3 are the calculated percentages of nitrogen. An amidine X:NY was prepared from the components XO and NH_2Y; *e.g.*,

NHPh·CMe:N·C_6H_4Me

from NHPh·COMe and $C_6H_4Me·NH_2$, and so on.

Formula.	M. p.	N %.	Remarks.
NHPh·CMe:N·C_6H_4Me (*m*).	103°	*12·7 (12·5)	Needles.
,, (*p*).	90	12·7	,,
,, (*o*).	138	12·9	Buff-coloured needles.
NHPh·CMe:N·$C_6H_4·NO_2$ (*p*).	189	16·9 (16·5)	Yellow, prismatic needles.†
NHPh·CMe:N·C_6H_4·OEt (*p*).	102	11·3 (11·0)	Colourless needles.

* C, 80·2 (80·3); H, 7·3 (7·1). † From methyl alcohol.

Formula.	M. p.	N %.	Remarks.
$NPh:CMe\cdot NPh_2$.	92	10·1 (9·8)	Prismatic needles.
(*m*) $C_6H_4Me\cdot NH\cdot CMe:NPh$.	103	12·8 (12·5)	Identical with the first.
(*m*) $C_6H_4Me\cdot NH\cdot CMe:N\cdot C_6H_4Me$(*o*).	101	12·1 (11·8)	Rectangular plates.
(*p*) ,, (*p*).	120	11·5	Needles.*
(*p*) $C_6H_4Me\cdot NH\cdot CMe:N\cdot C_6H_4\cdot NO_2$ (*m*).	134	15·9 (15·6)	Product boiled with water before crystallisation. Yellow needles.*
(*p*) $C_6H_4Me\cdot N:CMe:NPh_2$.	122	9·4 (9·3)	Needles.
(*p*) $OEt\cdot C_6H_4\cdot NH\cdot CMe:N\cdot C_6H_4\cdot OEt$ (*p*).	117	9·6 (9·6)	,,
$NHPh\cdot CPh:N\cdot C_6H_4Me$ (*o*).	107	10·0 (9·8)	,,
(*p*) $C_6H_4Br\cdot NH\cdot CMe:N\cdot C_6H_4Me$ (*o*).	122	9·4 (9·2)	Elongated needles.
$NPhMe\cdot CMe:N\cdot C_6H_4Me$ (*m*). (picrate)	157	15·2 (15·0)	The base is an oil. Isolated as the picrate. Bright yellow needles. The free base regenerated from the picrate is an oil which could not be solidified.
(*p*) $NO_2\cdot C_6H_4\cdot NH\cdot CMe:NPh$.	189	—	Mixed with the fourth compound, no lowering of m. p. observed.
$NHPh\cdot CMe:NPh$.	—	—	From acetanilide and phenylhydrazine.

* From dilute alcohol.

We wish to thank Professor R. Robinson, F.R.S., for his kind help in the preparation of the manuscript.

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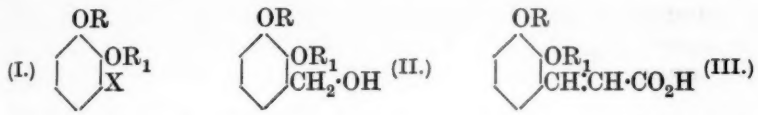
THE UNIVERSITY, MANCHESTER. [*Received, November 28th*, 1925.]

LXXXIX.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part IV.*

By LEON RUBENSTEIN.

THE investigation of substitution in dialkyloxybenzene derivatives of type (I) in which the group X is meta-directing has been conducted on a large number of compounds and discussed at length (Davies and Rubenstein, J., 1923, **123**, 2839; Rubenstein, J., 1925, **127**, 2268).* The continuation of that work is now described.

* The bromination of these dialkyloxyaldehydes has been stated (*loc. cit.*) to give only the 5-bromo-derivative, the argument being based upon (i) the position of substitution of the salicylaldehyde derivatives and (ii) the capacity of the brominated product to give a 6-nitro-compound. The position of the bromine atom in these compounds has now been proved by the direct preparation of 5-bromo-*o*-veratric acid from 5-nitro-*o*-veratric acid (see p. 652).



Substitution processes have been investigated on vicinal substances of type (I) in which X is a weakly ortho-para-orienting group. The first series of compounds examined as fulfilling these requirements were the dialkyloxybenzyl alcohols, and the nitration and bromination of these substances were carried out. In the nitration of *o*-veratryl alcohol, 2 : 3-diethoxybenzyl alcohol, and 3-methoxy-2-ethoxybenzyl alcohol good yields of the 5-nitro-benzyl alcohol were obtained in each case, the position of the nitro-group being shown by oxidation of the benzyl alcohol derivative to the corresponding benzoic acid. Bromination did not proceed so smoothly, but moderate yields of the 5-bromo-benzyl alcohols were obtained, the place of substitution again being shown by oxidation. The second series of compounds examined were the dialkyloxycinnamic acids (III) in which the group X (I) is ortho-para-orienting and unsaturated. In this case again, 5-nitro-derivatives were produced exclusively in the case of 2 : 3-diethoxycinnamic and 3-methoxy-2-ethoxycinnamic acids. From these substances, the respective benzoic acids were reformed on oxidation. From 2 : 3-dimethoxycinnamic acid a mixture of isomerides was formed on nitration, and by fractionally separating first the acids and then the esters left in the residual mixture on esterification it was shown that 85% of the nitration mixture consisted of 5-nitro-2 : 3-dimethoxycinnamic acid, the rest being the 6-nitro-acid.

EXPERIMENTAL.

5-Nitro-2 : 3-dimethoxybenzyl Alcohol.—2 : 3-Dimethoxybenzyl alcohol (5·5 g.; prepared from *o*-veratraldehyde by means of the Cannizzaro reaction) dissolved in glacial acetic acid (20 c.c.) is treated gradually with a solution of nitric acid (5·5 c.c., *d* 1·42) in glacial acetic acid (5·5 c.c.); the temperature rises to 40—50°. After being maintained at 50° for 2 hours and at room temperature over-night, the brown solution is poured into water. The product, an oil which slowly solidifies, crystallises from methyl alcohol in colourless needles, m. p. 67° (yield 90%) (Found : N, 6·6. $C_9H_{11}O_5N$ requires N, 6·6%). On oxidation with alkaline permanganate solution and subsequent acidification with dilute hydrochloric acid 5-nitro-*o*-veratric acid is obtained, m. p. 176°, identical with the acid obtained by the nitration of *o*-veratric acid.

3-Methoxy-2-ethoxybenzyl Alcohol.—3-Methoxy-2-ethoxybenzaldehyde (12 g.) dissolved in methyl alcohol (16 c.c.) is treated with

a solution of potassium hydroxide (17·6 g.) in methyl alcohol (45 c.c.). After 24 hours, the greater portion of the methyl alcohol is distilled off, the residue shaken with benzene, the extract washed a few times with concentrated sodium bisulphite solution and dried over potassium carbonate, and the benzene evaporated. The residual oil almost wholly distills at reduced pressure as a colourless liquid, b. p. 148°/13 mm. (yield, almost theoretical).

5-*Nitro*-3-*methoxy*-2-*ethoxybenzyl Alcohol*.—3-Methoxy-2-ethoxybenzyl alcohol (2 g.) dissolved in glacial acetic acid (2 c.c.) is treated with a solution of nitric acid (2 c.c.) in glacial acetic acid (2 c.c.), and the reddish-brown solution kept over-night. The 5-nitro-3-methoxy-2-ethoxybenzyl alcohol which separates in pale yellow, prismatic crystals is filtered off; more is obtained on pouring the filtrate into water and crystallising the oily product, which hardens, from alcohol; m. p. 132° (yield 65%) (Found : N, 6·4. $C_{10}H_{13}O_5N$ requires N, 6·2%). On oxidation with an alkaline solution of potassium permanganate 5-nitro-3-methoxy-2-ethoxybenzoic acid, m. p. 169°, is obtained.

2 : 3-*Diethoxybenzyl Alcohol*.—This is obtained from 2 : 3-diethoxybenzaldehyde and purified substantially by the process described under 3-methoxy-2-ethoxybenzyl alcohol. It is a colourless oil, b. p. 163°/11 mm., 167°/19 mm., which solidifies on cooling and can be crystallised from light petroleum (b. p. 60—80°), separating in colourless needles, m. p. 35° (Found : C, 67·6; H, 8·0. $C_{11}H_{16}O_3$ requires C, 67·4; H, 8·2%).

5-*Nitro*-2 : 3-*diethoxybenzyl Alcohol*.—This is obtained from 2 : 3-diethoxybenzyl alcohol (1·5 g. in glacial acetic acid, 2 c.c.) and nitric acid (1·5 c.c. in glacial acetic acid, 1·5 c.c.) by the method described under 5-nitro-2 : 3-dimethoxybenzyl alcohol. It crystallises from alcohol in colourless needles, m. p. 75° (yield 1·7 g. or 90%) (Found : N, 7·2. $C_{11}H_{15}O_5N$ requires N, 7·1%), and on oxidation with 1% alkaline permanganate yields 5-nitro-2 : 3-diethoxybenzoic acid, m. p. 118°, identical with the nitration product of 2 : 3-diethoxybenzoic acid.

5-*Bromo*-2 : 3-*dimethoxybenzyl Alcohol*.—*o*-Veratryl alcohol (5 g.), dissolved in glacial acetic acid (25 c.c.) containing sodium acetate (7·5 g.), is treated with bromine (5 g.) in glacial acetic acid (20 c.c.). After 2 days, the mixture is poured into water. The oil that separates, and hardens slowly, is removed (3·5 g.), and the filtrate treated with solid sodium bicarbonate; a further 3·7 g. of solid are then obtained. The combined products, crystallised from light petroleum a few times, yield 5-*bromo*-2 : 3-*dimethoxybenzyl alcohol* in colourless needles, m. p. 82° (Found : Br, 31·8. $C_9H_{11}O_3Br$ requires Br, 32·1%). The acid produced by its oxidation with

1% alkaline potassium permanganate at 60—70°, after crystallisation from light petroleum, melts at 120° and does not depress the m. p. of 5-bromo-*o*-veratric acid obtained by oxidation of 5-bromo-*o*-veratraldehyde.

5-Bromo-3-methoxy-2-ethoxybenzyl Alcohol.—3-Methoxy-2-ethoxybenzyl alcohol (2 g.) is brominated by the foregoing method. The oil produced on dilution, after hardening, is isolated by means of benzene and crystallised twice from light petroleum (b. p. 60—80°); *5-bromo-3-methoxy-2-ethoxybenzyl alcohol* is thus obtained in white prisms, m. p. 55—56° (Found: Br, 30·3. $C_{10}H_{13}O_3Br$ requires Br, 30·6%).

5-Bromo-2 : 3-diethoxybenzyl Alcohol.—2 : 3-Diethoxybenzyl alcohol (2·5 g.) dissolved in glacial acetic acid (13 c.c.) containing sodium acetate (4 g.) is treated at 20—25° with bromine (2 g.) in glacial acetic acid (7 c.c.). After remaining in sunlight for a few days, the mixture is poured into water; the oil obtained partly solidifies after several days. The oily portion is removed as completely as possible, and the residue crystallised three times from light petroleum; *5-bromo-2 : 3-diethoxybenzyl alcohol* is thus obtained in colourless, prismatic crystals, m. p. 60° (Found: Br, 28·6. $C_{11}H_{15}O_3Br$ requires Br, 29·1%).

Nitration of 2 : 3-Dimethoxycinnamic Acid.—The finely powdered acid (5 g.) is added in small portions and with stirring to nitric acid (25 c.c.; *d* 1·42). After 3 hours, the mixture is poured over ice. The cream-coloured precipitate (6 g.) is dried and dissolved in boiling alcohol. By careful fractional separation 3·3 g. of a substance, m. p. 205—227°, are obtained. The alcoholic filtrate is evaporated to small bulk, saturated with hydrogen chloride, and heated on a water-bath for 1 hour. Fractional separation of the mixture of esters thus produced yields first *ethyl 5-nitro-2 : 3-dimethoxycinnamate*, which crystallises from alcohol in cream, prismatic needles, m. p. 111° (Found: N, 5·2. $C_{13}H_{15}O_6N$ requires N, 5·0%). [*5-Nitro-2 : 3-dimethoxycinnamic acid* is obtained, by twice crystallising the product, m. p. 205—227°, in pale yellow prisms, m. p. 229° (Found: equiv., 256. $C_{11}H_{11}O_6N$ requires equiv., 253). Oxidation with potassium permanganate gives 5-nitro-*o*-veratric acid.] *Ethyl 6-nitro-2 : 3-dimethoxycinnamate* is obtained from later fractions and crystallises from aqueous alcohol in long, white needles, m. p. 86°. It is hydrolysed by boiling for a few minutes with equal volumes of water, glacial acetic acid, and sulphuric acid, giving *6-nitro-2 : 3-dimethoxycinnamic acid*, which crystallises from aqueous alcohol in brown needles, m. p. 210—215° (decomp.). On oxidation with alkaline potassium permanganate solution at 90° and acidification, it gives a substance of high m. p.

(above 280°) which appears to be identical with the 6-*nitro*-3-*hydroxy*-2-*methoxybenzoic acid* obtained by boiling 6-nitro-2 : 3-dimethoxybenzoic acid for 15 hours with 2·5 *N*-sodium hydroxide.

3-*Methoxy*-2-*ethoxycinnamic Acid*.—3-Methoxy-2-ethoxybenzaldehyde (6 g.) is added to pyridine (20 c.c.) containing malonic acid (7·2 g.), 6 drops of piperidine are added, and the solution is heated under reflux on a steam-bath for 1 hour; the evolution of carbon dioxide is then completed by boiling the solution for 5 minutes. The cooled solution is poured into water acidified with concentrated hydrochloric acid, and the precipitate of 3-methoxy-2-ethoxycinnamic acid (yield almost quantitative) collected. It crystallises from alcohol in colourless needles, m. p. 151° (Found: equiv., 220. $C_{12}H_{14}O_4$ requires equiv., 222).

5-*Nitro*-3-*methoxy*-2-*ethoxycinnamic Acid*.—Finely divided 3-methoxy-2-ethoxycinnamic acid (1 g.) is added gradually to nitric acid (10 c.c.; *d* 1·42), and the mixture kept over-night. On dilution with water 5-*nitro*-3-*methoxy*-2-*ethoxycinnamic acid* is obtained in quantitative yield. Crystallised from alcohol, it gives cream needles, m. p. 200—201° (Found: equiv., 269. $C_{12}H_{13}O_6N$ requires equiv., 267).

2 : 3-*Diethoxycinnamic Acid*.—This acid, prepared from 2 : 3-diethoxybenzaldehyde (5 g.) by the pyridine method described above (yield 5·3 g. or 90%), crystallises from alcohol in long, slender, colourless needles, m. p. 161° (Found: equiv., 235. $C_{13}H_{16}O_4$ requires equiv., 236).

5-*Nitro*-2 : 3-*diethoxycinnamic Acid*.—Prepared (at 20—25°) from 2 : 3-diethoxycinnamic acid (1 g.) and isolated by the method described under 5-nitro-3-methoxy-2-ethoxycinnamic acid, this acid is obtained in quantitative yield. It crystallises in long, cream prisms, m. p. 199° (Found: equiv., 280·5. $C_{13}H_{15}O_6N$ requires equiv., 281).

The following is an account of the preparation of 5-bromo-*o*-veratric acid from 5-nitro-*o*-veratric acid.

5-Nitro-2 : 3-dimethoxybenzoic acid (4·5 g.) is heated with concentrated hydrochloric acid (15 c.c.) and tin (4·5 g.) on a steam-bath for a few hours, the solution diluted with water, the tin removed as sulphide, and the colourless filtrate evaporated under reduced pressure; white, prismatic crystals of the hydrochloride of 5-amino-2 : 3-dimethoxybenzoic acid are deposited (yield 80%).

The hydrochloride is soluble in water or alcohol and in warm concentrated hydrochloric acid, from which it can be crystallised. The solutions turn pink and then red in the air, especially if in presence of an excess of acid. 5-Amino-2 : 3-dimethoxybenzoic acid is obtained by treating a concentrated solution of the hydrochloride

with solid sodium carbonate until it is just acid to Congo-red. The colourless needles, m. p. 250° (decomp.), soon become deep-red owing to oxidation, and are soluble in acids and in alkalis (Found : N, 6·9. $C_9H_{12}O_4N$ requires N, 7·0%).

The hydrochloride (4 g.) is dissolved in water (17 c.c.), neutralised with solid sodium carbonate, treated with hydrobromic acid (7·5 c.c.; *d* 1·50), and diazotised at 0° with sodium nitrite (1·2 g. in water, 3 c.c.). The black, semi-crystalline solid obtained by heating the diazonium solution with cuprous bromide and concentrated hydrobromic acid is boiled with alcohol and animal charcoal, and the hot filtered solution cooled after addition of a little water. Long, cream needles are deposited, m. p. 112—113°, which, after further treatment with animal charcoal and recrystallisation from aqueous alcohol, melt at 120° and do not depress the m. p. of 5-bromo-*o*-veratric acid obtained by oxidation of 5-bromo-*o*-veratraldehyde.

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THE DYSON PERRINS LABORATORY,
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XC.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part II. The Influence of the Hydroxy-compound.*

By TUDOR WILLIAMS PRICE.

IN Part I (J., 1924, **125**, 115) an account was given of the reaction between phenylmethylcarbamyl chloride and ethyl alcohol at different temperatures. An account is now given of the reaction between phenylmethylcarbamyl chloride and various hydroxy-compounds at 100°.

Norris and Ashdown (*J. Amer. Chem. Soc.*, 1925, **47**, 837) studied the reaction between various alcohols and *p*-nitrobenzoyl chloride in ether at 25°, but no quantitative work, so far as the author is aware, has hitherto been published on the influence of the constitution of the hydroxy-compound upon the velocity of reaction with a carbamyl chloride.

Materials.—The phenylmethylcarbamyl chloride was from the same batch as was used in the previous work, and had been kept over phosphoric oxide in a desiccator.

The various alcohols used were the purest commercial alcohols

and were all treated twice at their respective boiling points with fresh calcium turnings (1·0 and 0·5% by weight) and fractionated. The other hydroxy-compounds, which also were the purest commercial substances, were purified by fractional distillation, some under reduced pressure. Each hydroxy-compound after purification boiled either constantly at one temperature or over a range of less than 0·2°.

Method of Work.—In each experiment, 0·424 g. of the carbamyl chloride (equivalent to 25 c.c. of *N*/10-solution) and 5 c.c. of the hydroxy-compound were sealed in a test-tube and heated at 100° for a definite time. A hydroxy-compound that was solid at the ordinary temperature was first melted and 5 c.c. were placed in the tube, which was then cooled before the carbamyl chloride was introduced. These proportions caused the hydroxy-compound to be present in large excess, thus making the reaction unimolecular with respect to the carbamyl chloride.

In the case of the alcohols the whole reaction is made up of two consecutive reactions :

$$(1)\ \mathrm{NMePh{\cdot}COCl} + \mathrm{ROH} = \mathrm{NMePh{\cdot}CO_2R} + \mathrm{HCl}$$
$$(2)\ \mathrm{HCl} + \mathrm{ROH} = \mathrm{RCl} + \mathrm{H_2O}$$

but the progress of the first reaction can be studied by determining the amount of carbamyl chloride left in the system at any instant. This was done, for those alcohols (methyl, ethyl, and *n*-propyl) which give low-boiling chlorides, in the manner described in Part I (*loc. cit.*). For the other hydroxy-compounds, since aspiration of air through the system would not remove the chloro-compound formed, the following method was used. After being heated at 100° for the required time, the mixture was titrated with *N*/10-potassium hydroxide. Excess of ammonia was then added to convert any unchanged carbamyl chloride into ammonium chloride and the corresponding substituted carbamide. The solution, after standing in the cold for 1 hour to complete the conversion, was extracted four times with light petroleum to remove the chloro-derivative of the hydroxy-compound, acidified with pure nitric acid, and titrated with *N*/10-silver nitrate without an indicator. This titre was a measure of both the ammonium chloride and the hydrogen chloride present. The amount of the latter was known from the *N*/10-potassium hydroxide titre, and by subtraction the ammonium chloride titre, which was equivalent to the carbamyl chloride, was obtained.

In the case of *n*-propyl alcohol both methods were employed, and gave almost identical results.

The quantity of phenylmethylcarbamyl chloride present being

known, the velocity coefficient for a unimolecular reaction was calculated from the expression

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where t_1 is 5 minutes and $a - x_1$ is the amount of carbamyl chloride present in the system after the tube had been in the water-bath at 100° for 5 minutes. This expression was used to obviate the initial disturbances.

Results.

In Table I, where the results for methyl and *n*-propyl alcohols are given in detail, the first column gives the duration of heating in minutes (*t*), the second the amount of hydrogen chloride present, expressed as c.c. of *N*/10-solution (*b*), the third the amount of hydrogen chloride plus phenylmethylcarbamyl chloride present, expressed as c.c. of *N*/10-solution (*c*). The fourth column gives the amount of phenylmethylcarbamyl chloride present (*d*), obtained by subtracting the figures in column 2 from those in column 3. The fifth column gives the velocity coefficient for the reaction between phenylmethylcarbamyl chloride and the hydroxy-compound, calculated from the figures in column 4.

The whole of the results are summarised in Table II.

TABLE I.

Methyl Alcohol.					n-*Propyl Alcohol.*				
t.	*b.*	*c.*	*d.*	*k.*	*t.*	*b.*	*c.*	*d.*	*k.*
5	12·44	23·52	11·00	—	5	1·46	25·02	23·56	—
6	13·83	22·57	8·74	0·237	10	3·96	24·90	20·94	0·0236
8	14·96	20·59	5·63	0·216	15	6·49	24·71	18·22	0·0257
10	15·05	18·61	3·56	0·227	20	8·14	24·48	16·34	0·0244
13	14·18	16·18	2·00	0·214	25	9·81	24·11	14·30	0·0250
15	13·06	14·34	1·28	0·216	35	11·98	23·15	11·17	0·0249
			Mean	0·222	45	13·76	21·96	8·20	0·0264
					60	14·74	20·47	5·73	0·0257
								Mean	0·0251

TABLE II.

Hydroxy-compound.	Limits of *k*.	Mean *k*.
$CH_3 \cdot OH$	0·237 —0·214	0·222
$C_2H_5 \cdot OH$	0·0437—0·0417	0·0427
n-$C_3H_7 \cdot OH$	0·0264—0·0236	0·0251
iso-$C_3H_7 \cdot OH$	0·0113—0·0099	0·0106
n-$C_4H_9 \cdot OH$	0·0188—0·0166	0·0177
iso-$C_4H_9 \cdot OH$	0·0158—0·0154	0·0156
iso-$C_5H_{11} \cdot OH$	0·0125—0·0121	0·0123
$CH_2Ph \cdot OH$	0·0198—0·0179	0·0185
$CH_2{:}CH \cdot CH_2 \cdot OH$	0·0448—0·0399	0·0420
$CHPh{:}CH \cdot CH_2 \cdot OH$	0·0078—0·0068	0·0074
PhOH	0·317 —0·290	0·308
o-$C_6H_4Me \cdot OH$	0·0567—0·0514	0·0541
m-$C_6H_4Me \cdot OH$	0·149 —0·139	0·146
p-$C_6H_4Me \cdot OH$	0·176 —0·169	0·175
$C_2H_4(OH)_2$	Too fast to measure accurately.	
$C_3H_5(OH)_3$	Did not dissolve the carbamyl chloride.	

The hydroxy-compound may influence the reaction in two ways: by its constitution and by its solvent action. The influence of a solvent on the velocity of a reaction in which it does not take part has been extensively studied, and no general relation has been traced between the chemical or physical properties of the solvent and its effect on the velocity coefficient.

Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611; 1890, **6**, 41) found that the velocity of certain reactions was greatest in those solvents having the highest dielectric constant, but in other reactions this rule did not hold. Patterson and Montgomerie (J., 1912, **101**, 26, 2100) state that a given set of solvents may hasten a particular reaction in a certain sequence, whilst it may retard another reaction in the same or nearly the same sequence, and that the properties which bring this about are probably the same throughout.

Another view of the influence of the solvent is that the solvent and the solute form an unstable additive compound, in which case it is probable that the chemical constitution of the solvent, rather than its physical properties, would be most effective in influencing the velocity of the reaction. The work of Cox (J., 1920, **117**, 493) supports this view.

In the present work, the hydroxy-compound, which can be regarded as a solvent, reacts with the carbamyl chloride, hence its chemical constitution does influence the velocity of the reaction and the question arises whether, in addition to that, the physical properties of the hydroxy-compound play a part. The physical properties most likely to have some effect upon the velocity of a reaction are the viscosity, the dielectric constant, and the refractive index.

Reformatsky (*Z. physikal. Chem.*, 1891, **7**, 34) showed that viscosity did not appear to have any great influence on the velocity coefficient of a reaction. The refractive index of the hydroxy-compounds examined varies between $n_D^{20^\circ}$ 1·3290 for methyl alcohol and $n_D^{26\cdot6^\circ}$ 1·576 for cinnamyl alcohol; for most of them it is about 1·4, so that the small differences in refractive index are not sufficient to explain the large differences in velocity coefficient. The dielectric constant shows a greater variation, the highest being 32 for methyl alcohol (20°) and the lowest 9·7 for phenol (48°). These two extremes, however, are the values for the hydroxy-compounds having the greatest velocity coefficients, so that there does not seem to be a connexion between dielectric constant and velocity coefficient. In addition, the differences between the physical properties of the various liquids will tend to become smaller as the temperature is raised and therefore it is probable that at 100° the effect due to the different solvent action of the hydroxy-compounds will be very

small compared with the effect of their differences in chemical constitution.

In considering the effect of chemical constitution upon the velocity of a reaction several factors have to be taken into account: first, the general polar effect, due to substituent atoms or groups affecting the molecule as a whole; secondly, the steric effect; and thirdly, an alternate polarity effect. In many cases two or all three factors may operate simultaneously, and then it is difficult to assess the effect of each factor individually. With regard to the straight-chain aliphatic primary alcohols, the steric factor is not sufficiently strong to influence the velocity, and the results show no trace of an alternate effect, for the velocity coefficients are in the order methyl alcohol > ethyl alcohol > *n*-propyl alcohol > *n*-butyl alcohol. The order is the same as that found by Menschutkin (*Z. physikal. Chem.*, 1887, **1**, 611) in the reaction between acetic anhydride and several alcohols in benzene solution at 100°, and different from that found by Norris and Ashdown (*loc. cit.*), where the order was methyl alcohol > ethyl alcohol > *n*-butyl alcohol > *n*-propyl alcohol. The reactivity of the alcohol decreases, *i.e.*, the hydroxyl hydrogen atom becomes more firmly bound, as the length of the straight chain increases. With the primary *iso*-compounds it is again seen that an extra $-CH_2-$ group in the straight chain decreases the velocity coefficient. A branched-chain alcohol has a smaller velocity coefficient than a straight-chain alcohol of the same molecular weight; thus *n*-propyl > *iso*propyl and *n*-butyl > *iso*butyl. In the case of *iso*propyl alcohol the velocity coefficient is abnormally small, probably owing to a steric effect superimposed upon the general polar effect of the substituent, since this is a secondary alcohol whilst the others are primary alcohols. A similar effect was found by Ashdown and Norris.

The introduction of a phenyl group at the end of the straight chain decreases considerably the reactivity of the alcohol, as is shown by the following figures: methyl alcohol 0·222, benzyl alcohol 0·0185, allyl alcohol 0·0420, cinnamyl alcohol 0·00744.

The effect of unsaturation is to cause a great increase in the reactivity of the alcohol; thus *n*-propyl alcohol 0·0251, allyl alcohol 0·0420.

Taking methyl alcohol as the standard, and considering the replacement of one of its hydrogen atoms in the methyl group, we find that the general polar effect of the various substituents in decreasing the reactivity of the hydroxyl hydrogen is in the following order: $CH_3 < CH_2{:}CH < C_2H_5 < C_6H_5 < C_3H_7 < CH(CH_3)_2 < CH(CH_3)_2{\cdot}CH_2 < C_6H_5{\cdot}CH{:}CH$.

The introduction of a second hydroxyl group, as in ethylene

glycol, increases the reactivity so greatly that the velocity coefficient cannot be obtained with accuracy by the method employed.

The aromatic compounds show special features. Phenol, as was to be expected, is very reactive, more so than methyl alcohol. The introduction of a methyl group, as in the cresols, diminishes the reactivity of the hydroxyl hydrogen, the extent of the diminution depending on the relative positions of the methyl and hydroxyl groups in the benzene ring. The velocity coefficients are: phenol 0·308, *o*-cresol 0·0541, *m*-cresol 0·146, *p*-cresol 0·175. The low value for *o*-cresol is undoubtedly due to a preponderating steric effect.

Work with other carbamyl chlorides is in progress.

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XCI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVIII.* d-sec.-*Butylbenzene.*

By PHILIP WILLIAM BENSON HARRISON, JOSEPH KENYON, and JOHN ROBERT SHEPHERD.

OF the compounds which have been examined in the study of the relationship between chemical constitution and optical activity, very few have been hydrocarbons, probably because of the experimental difficulties in preparing this type of compound in an optically active condition.

Mention may be made, however, of *d*-methylethyl-*n*-propylmethane with $[\alpha]_D^{20°}$ + 9·5°, which was prepared by Marckwald (*Ber.*, 1904, **37**, 1046) by the action of sodium on a mixture of ethyl iodide and *d*-amyl iodide. Klages and Sautter (*Ber.*, 1904, **37**, 649) prepared *d*-α-phenyl-γ-methylpentane ($[\alpha]_D^{14·5°}$ + 17·2°) by the reduction of *d*-α-phenyl-γ-methyl-Δ^{α}-pentene ($[\alpha]_D^{12°}$ + 43°), which was obtained by the interaction of active amyl iodide ($[\alpha]_D^{18°}$ + 5·78°) and benzaldehyde in presence of magnesium. The same authors (*Ber.*, 1905, **38**, 2312), by analogous reactions, prepared *d*-γ-*m*-*iso*propylphenyl-γ-methylpentane ($[\alpha]_D^{15·5°}$ + 15·91°) and *d*-γ-*m*-*iso*propylphenyl-γ-methyl-Δ^{α}-pentene ($[\alpha]_D^{16°}$ + 41·89°).

This communication describes the preparation of *sec.*-butylbenzene in what is believed to be an optically pure condition.

The preparation has proved to be so tedious and laborious that the question of preparing other optically active hydrocarbons will be held in abeyance until a more convenient procedure has been devised.

The method of preparing *d-sec.*-butylbenzene is briefly as follows : The inactive hydrocarbon was nitrated and the *p*-nitro-*sec.*-butylbenzene, which is the principal product of the reaction, was reduced to *p*-amino-*sec.*-butylbenzene. The latter was then converted into the *hydrogen tartrate*, which was submitted to systematic prolonged fractional crystallisation until a salt of constant rotatory power was obtained. The amino-group of the optically active base obtained by the decomposition of this salt was then eliminated in the usual way, giving optically active *sec.*-butylbenzene.

The resolution of *sec.*-butylbenzene into its optically active isomerides had been attempted previously. Klages (*Ber.*, 1906, **39**, 2131) converted the hydrocarbon into its sulphonic acid and obtained therefrom a number of crystalline salts by combining it with several of the commoner alkaloids. Fractional crystallisation of these salts, however, brought about no resolution.

p-Amino-*sec.*-butylbenzene was obtained in an optically active condition by Glattfeld and Wertheim (*J. Amer. Chem. Soc.*, 1921, **43**, 2682) by the crystallisation of the salt with *d*-camphorsulphonic acid. The rotatory power of the amine quoted by these authors is, however, far too low, being some sixty times smaller than the value obtained in the course of the present work.

Each of the compounds now described exhibits a very high optical rotatory dispersive power: $\alpha_{4359}/\alpha_{5461} = 1{\cdot}87$ for the amine and 1·81 for the hydrocarbon, whilst an examination of the rotatory powers shows that in no case do they satisfy the simple dispersion equation $\alpha = K/(\lambda^2 - \lambda^2_0)$.

As it is possible that the high optical rotatory dispersive power may be due to these compounds containing a benzene nucleus in the molecule, several attempts were made to reduce *sec.*-butylbenzene to *sec.*-butyl*cyclo*hexane to ascertain what effect, if any, the loss of aromatic character would have on the rotatory dispersive power. However, under the conditions employed, namely, agitation of the substance with hydrogen in the presence of colloidal platinum or palladium, little, if any, reduction was effected.

Experimental.

dl-sec.-Butylbenzene was prepared by the method of Klages (*Ber.*, 1902, **35**, 2641). The methylethylphenylcarbinol obtained by the interaction of magnesium ethyl chloride and acetophenone was slowly distilled at the ordinary pressure, and the resulting

β-phenyl-Δ^{β}-butylene (75% yield) reduced rapidly with sodium and absolute alcohol. *sec.*-Butylbenzene was collected at 168—173° and obtained in 87% yield.

p-*Nitro*-sec.-*butylbenzene*.—To *dl-sec.*-butylbenzene (200 g.) was added during 3 hours a mixture of nitric acid (128 c.c.; *d* 1·42) and sulphuric acid (160 c.c.; *d* 1·84) at such a rate that the temperature of the reaction was maintained at 15—20°; external cooling was resorted to, and the mixture kept vigorously stirred. The principal product of the reaction was *p*-nitro-*sec.*-butylbenzene —shown by the production of *p*-nitrobenzoic acid in good yield on oxidation—accompanied by a relatively small amount of a lower-boiling fraction which was presumably *o*-nitro-*sec.*-butylbenzene. Only a rough separation was possible at this stage, owing to the difficulty of obtaining a fraction of constant boiling point. Further purification was, however, easily effected after the next operation by the recrystallisation of the *oxalates* of the mixed amines.

dl-p-*Amino*-sec.-*butylbenzene*.—The *p*-nitro-compound was very easily reduced to the corresponding amine by tin and concentrated hydrochloric acid. After decomposition of the stannic chloride compound of the base by caustic soda, the amine was isolated by distillation in steam.

The mixture of neutral oxalates of the amines was crystallised several times from hot water and it was found by determining the density of the amine recovered that one crystallisation was sufficient to remove almost completely the lower-boiling isomeride of greater density. The amine thus obtained distilled constantly at 118°/15 mm.; its density ($d_4^{15°}$ 0·949), and the melting point (123°) of its acetyl derivative were unaltered after further recrystallisation of the neutral oxalate. Reilly and Hickinbottom (J., 1920, **117**, 120) give 125—126° as the melting point of *p-sec.*-butylacetanilide; that prepared by the present authors melts at 123° even after several recrystallisations.

Resolution of dl-p-*Amino*-sec.-*butylbenzene*.—Salts of the *dl*-amine with several optically active acids were prepared—that with *l*-malic acid was excessively soluble and could not be crystallised; those with *d*-camphoric and *d*-camphorsulphonic acids were crystalline, but their separation into enantiomorphous forms by fractional crystallisation was too slow to be of use. The compound with *d*-hydroxymethylenecamphor was also prepared, but fractional crystallisation of this failed to effect any resolution. (This is in agreement with the observation of Glattfeld and Wertheim, *loc. cit.*).

After many preliminary attempts it was found that the *d*-hydrogen

tartrate was the most promising of all the salts tried. *p*-Amino-*sec.*-butylbenzene (285 g.) was added to a hot solution of *d*-tartaric acid (300 g.) in water (1100 c.c.); the clear solution on standing deposited a crop of crystals (which titration showed to be the *hydrogen tartrate*) in very small, prismatic rods. These were systematically recrystallised until the rotatory power of the amine obtained by decomposing successive crops of the crystals became constant. The rate of the resolution is indicated by the following data:

After four recrystallisations of the hydrogen tartrate, the observed rotatory power ($\alpha^{20°}_{5461}$; $l = 100$ mm.) of the liberated base was + 16°, after eight + 23°, after twelve + 28°, after sixteen + 31°, after twenty-two + 37°, after twenty-five + 38·2°, after twenty-seven + 38·7°, after thirty + 38·7°.

This prolonged process of recrystallisation is very wasteful and the *d*-*p*-amino-*sec.*-butylbenzene obtained by decomposition of the various crops of salt of constant rotatory power amounted to only 10 g. The amine had b. p. 114°/12 mm. and $d^{20°}_{4}$ 0·945.

Various attempts were made to isolate the lævorotatory form of *p*-amino-*sec.*-butylbenzene in an optically pure condition, but without success. By the decomposition of the most soluble fractions of the hydrogen tartrate, portions of amine of rotatory powers lying between α_{5461} — 12° and — 20° were obtained. The *d*-camphorsulphonate of the base with α_{5461} — 20° was prepared and recrystallised several times; the lævorotation of the amine obtained from the less soluble fractions of this salt increased, but at so slow a rate as to render the method valueless. Recrystallisation of the hydrochloride and of the oxalate of the partially active amine was also without effect on the rotatory power. Other solvents besides water were tried in all the above cases for recrystallisation of the various salts, but they bring about separation with even greater slowness than does water.

d-sec.-*Butylbenzene* was readily prepared by mixing a solution of *d*-*sec.*-butylbenzenediazonium chloride (from 6 g. of amine) with a strongly alkaline solution of sodium stannite and distilling the mixture in a current of steam. The hydrocarbon was obtained as a colourless liquid which distilled constantly at 172°; the yield was 2 g. = 40% of the theoretical (compare Friedländer, *Ber.*, 1889, **22**, 587).

Although it was considered unlikely that any racemisation would occur during the elimination of the amino-group situated at the end of the molecule remote from the asymmetric carbon atom, yet the following experiments were carried out to gain some information on this important point. Partially active *d*- and *l*-*p*-amino-*sec.*-butylbenzenes of various degrees of rotatory power were diazotised

Determinations of Rotatory Power.

d-p-*Amino*-sec.-*butylbenzene*. $d_{4}^{20°}$ 0·9449.

Solvent.	G. of solute in 100 c.c. of soln.	*l* in mm.	$\alpha_{\lambda}^{20°}$ Observed. λ. 6708.	5896.	5790.	5461.	4359.	$[\alpha]_{\lambda}^{20°}$. λ. 6708.	5896.	5790.	5461.	4359.
Homogeneous	—	25	+5·85°	+8·00°	+8·37°	+9·68°	+18·10°	+24·75°	+33·86°	+35·42°	+40·98°	+76·6°
Ethyl alcohol	4·94	100	1·31	1·76	—	2·05	3·75	26·5	35·6	—	41·5	75·8
Carbon disulphide ...	5·01	100	1·45	2·00	—	2·44	4·96	28·9	39·9	—	48·7	99·0
Chloroform	5·02	100	1·15	1·63	1·72	2·00	3·72	22·9	32·5	34·3	39·8	74·1
d-p-sec.-*Butylacetanilide*. M. p. 124°.												
Chloroform	4·99	100	0·97	1·34	1·40	1·58	2·90	19·4	26·8	28·0	31·6	58·1
d-sec.-*Butylbenzene*. $d_{4}^{20°}$ 0·8639.												
Homogeneous	—	25	4·41	5·90	6·19	7·14	12·96	20·42	27·31	28·66	33·15	60·0

	Density.			*Refractive Index* ($n_{\lambda}^{25°}$). λ. 6708.	5896.	5790.	5461.	4359.
d-sec.-*Butylbenzene*	$d_{4}^{15°}$ 0·8681,	$d_{4}^{20°}$ 0·8639,	$d_{4}^{25°}$ 0·8590.	1·4838	1·4883	1·4890	1·4915	1·5061
d-p-*Amino*-sec.-*butylbenzene*	$d_{4}^{15°}$ 0·9475,	$d_{4}^{20°}$ 0·9449,	$d_{4}^{25°}$ 0·9411.	1·5284	1·5346	1·5356	1·5391	1·5589
dl-p-*Nitro*-sec.-*butylbenzene*	$d_{4}^{20°}$ 1·063.			—	—	1·5322	1·5363	1·5622

and treated with sodium stannite under different experimental conditions; the ratio of the rotatory power of the original amine to that of the hydrocarbon obtained from it in each of the several cases was quite constant, thus rendering it highly improbable that any racemisation had taken place.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant with which some of the materials used in this investigation were purchased. Two of them (J. R. S. and P. W. B. H.) wish also to acknowledge their indebtedness to the Department of Scientific and Industrial Research for maintenance grants which enabled them to participate in the work.

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XCII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part VI. Some Reactions of* iso*Phorone.*

BY JOHN WILLIAM BAKER.

THE chemistry of homocyclic compounds is often complicated by reactions which find no simple explanation in the structure usually assigned to the compound (Farmer and Ingold, J., 1920, **117**, 1362, and subsequent papers), the ambiguity extending in one case even to the synthesis of the substance, syntheses which should yield respectively the acids (I) and (II) yielding the same acid (Farmer, Ingold, and Thorpe, J., 1922, **121**, 128).

(I.) $Me_2C<^{C(CO_2H)\cdot CH_2}_{CH\text{——}CO}$ $\qquad$ $Me_2C<^{C(CO_2H):CH}_{CH_2\text{——}CO}$ (II.)

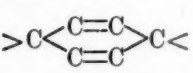
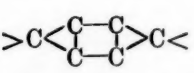
Such conflicting evidence was reconciled by the assumption of intra-annular tautomerism between the *bicyclo*pentene and the *cyclo*pentadiene systems, the two enolic forms being merely valency isomerides in accordance with the scheme :

$$Me_2C<^{C(CO_2H):CH}_{CH=\!=\!=C\cdot OH} \rightleftharpoons Me_2C<^{C(CO_2H)\cdot CH}_{CH\text{——}C\cdot OH}$$

There is no *a priori* reason why such redistribution of residual affinity within the ring, extending from mere conjugation of affinity across the ring to the establishment of a real bridge bond, should be restricted to the *cyclo*pentadiene series : its extension to the

heterocyclic rings thiophen and furan, and to benzene has already been developed (Ingold, J., 1922, **121**, 1133, and subsequent papers).

The present paper deals with the extension of such intra-annular tautomerism to the *cyclo*hexadiene series in accordance with the general scheme :

(III.)   (IV.)

On first inspection it may be considered that the structure (IV) is improbable in view of the strain involved, but it must be understood that it is not intended to represent a stable individual substance, but merely a phase in the scheme of valency distribution which, under favourable conditions, may pass into a more stable, true bridged phase. Such favourable conditions may occur when one or both of the potential trimethylene rings are stabilised by the presence of a *gem*-dimethyl group, and, in this case, products containing a *cyclo*propane ring may result from the degradation of the molecule.

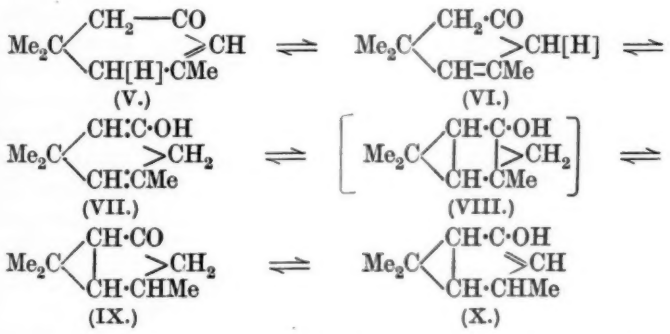
An example of this type of intra-annular tautomerism has, in the author's opinion, been established in the case of *iso*phorone. The generally accepted formula (V) for *iso*phorone has been established both by synthesis and by oxidation. Knoevenagel and Fischer (*Annalen*, 1897, **297**, 185) obtained it by the condensation of mesityl oxide and ethyl acetoacetate at 5° and hydrolysis of the *iso*phoronecarboxylic ester so produced. The structure was confirmed by Crossley and Gilling (J., 1909, **95**, 24), who obtained the ketone by the condensation of ethyl sodiomalonate with chlorodimethyl*cyclo*hexenone and hydrolysis of the ethyl dimethyl*cyclo*hexenoneacetate so obtained.

The oxidation of *iso*phorone was investigated by Bredt and Rubel (*Annalen*, 1898, **299**, 160), who obtained a whole series of acids intermediate between *iso*phorone and its final oxidation product, *as*-dimethylsuccinic acid. Formula (V) is also in good accord with most of the reactions of the ketone, *e.g.*, the formation of monobenzylidene-monopiperonylidene derivatives.

Kerp and Muller (*Annalen*, 1898, **299**, 193), however, found that this structure alone was not sufficient to represent all the reactions of *iso*phorone (obtained, in this case, by the condensation of acetone). *iso*Phorone condenses with another molecule of acetone to yield a higher condensation product, xylitone, which these investigators found also yields a monobenzylidene derivative, and hence must contain the group $CMe_2{:}C{\cdot}CO{\cdot}CH_2{\cdot}$; this necessarily involves the existence of the group $\cdot CH_2{\cdot}CO{\cdot}CH_2\cdot$ in the original *iso*phorone molecule. Hence, in this reaction at least, *iso*phorone

must be represented by the structure (VI) rather than (V), and these authors concluded that *iso*phorone obtained from acetone is a static mixture of the two isomerides (V and VI).

The interconversion of these two forms merely involves the well-known $\alpha\beta$–$\beta\gamma$ change across a three-carbon system, and the conflicting results would be readily explained if such a tautomeric system were assumed to exist in the *iso*phorone molecule. The enolic modification (VII) of the structure (VI) conforms to the *cyclo*hexadiene type mentioned above, and hence there is the possibility of a second kind of tautomeric change, *viz.*, intra-annular, a redistribution of affinity across the ring resulting, initially, in the tri*cyclo*hexane structure (VIII). It is not suggested that this form represents more than a transitory phase in the whole scheme, for only one of the potential three-membered rings is stabilised by the presence of a *gem*-dimethyl group, and it is to be expected that such a structure would immediately ketonise across the ring, thus destroying the unstabilised three-membered ring, to yield a bridged modification of the *iso*phorone molecule (IX). Finally, this could change in the usual manner to yield an enolic modification of a bridged form of *iso*phorone. The complete scheme is as follows :

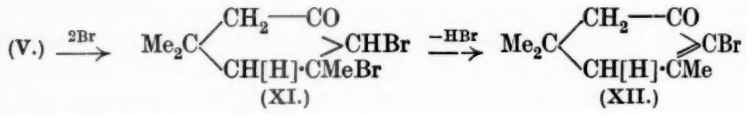


Thus in the *iso*phorone molecule three types of tautomerism are possible, each being superimposed on the other; (*a*) three-carbon, $\alpha\beta$–$\beta\gamma$-change, (*b*) intra-annular, (*c*) keto-cyclol.

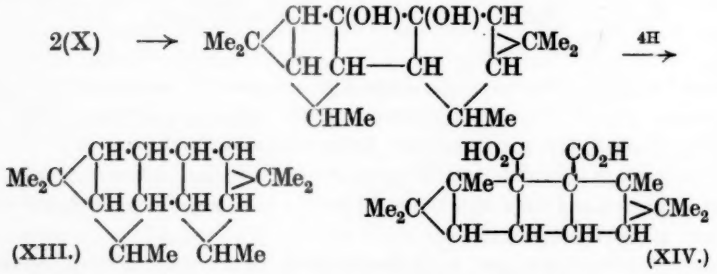
Evidence is submitted in this paper which, in the author's opinion, can be explained only by assuming such a scheme in connexion with the *iso*phorone molecule.

Kerp and Muller (*loc. cit.*) found that in ice-cold glacial acetic acid solution *iso*phorone forms an unstable dibromo-additive product which spontaneously evolves hydrogen bromide. Their analysis is 5% low for this compound. When, however, *iso*phorone in ice-cold carbon tetrachloride solution is treated with a standard

solution of bromine in the same solvent, absorption is rapid and a white, crystalline dibromo-compound (XI) separates, but no trace of hydrogen bromide is evolved until two atoms of bromine have been added. This additive compound is stable in the absence of moisture, but on exposure to air it immediately loses one molecule of hydrogen bromide to form monobromo*iso*phorone (XII). Although the possibility of bromine addition to the enolic double bond and subsequent loss of hydrogen bromide to yield a α-bromoketone cannot be excluded, it is considered more probable, in view of the degree of stability of the intermediate compound, that the addition of bromine occurs at the double bond in the three-carbon system, thus forming a blocked system, which therefore spontaneously liberates hydrogen bromide to reform a mobile system in accordance with the scheme :



Evidence of the bridged modification of *iso*phorone was obtained by a study of its reduction products. When *iso*phorone is reduced by the Clemmensen method, a solid hydrocarbon, $C_{18}H_{28}$, can be isolated in small yield from the product. This hydrocarbon is saturated, and therefore valency considerations necessitate the existence of the bridged structure (XIII). This structure is supported by the oxidation of the hydrocarbon with boiling potassium permanganate in sodium hydrogen carbonate suspension, the main product being *trans*-caronic acid. The formation of this hydrocarbon from the bridged, enolic modification of *iso*phorone (X) is represented by the following scheme, additive ring formation preceding the reduction :

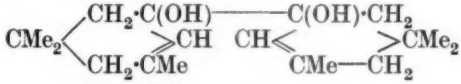


A similar constitution has been assigned to α-dicamphylic acid (XIV) obtained by the action of potash on sulphocamphylic acid (Perkin, J., 1903, **83**, 835).

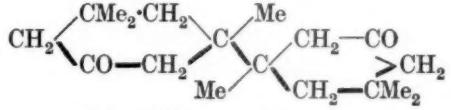
Reduction of *iso*phorone with sodium and moist ether yields a

mixture of two isomerides, $C_{18}H_{30}O_2$, m. p. 126° and 162°, respectively. The latter is undoubtedly the product obtained by Hess and Munderloh (*Ber.*, 1916, **51**, 383) by the reduction of *iso*phorone with 2·5% sodium amalgam and methyl alcohol. These investigators, apparently merely on the analytical data, assigned the pinacol formula (XV) to this product. Such a constitution is, however, quite inconsistent with the properties of this reduction product. Both substances, m. p. 126° and 162°, are saturated and do not decolorise potassium permanganate in sodium hydrogen carbonate solution in the cold, both yield disemicarbazone derivatives, but neither will form an acetyl derivative on heating with acetic anhydride. They are probably derived from the unsaturated ring form of *iso*phorone (VII) by a reduction similar to that which occurs in the formation of deoxymesityl oxide and deoxyphorone, respectively, from mesityl oxide and phorone, two stereoisomerides (XVI and XVII) being produced.

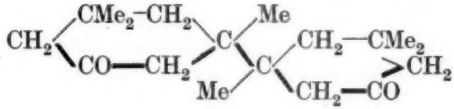
(XV.)



(XVI.)



(XVII.)



Thus the ambiguity of structure which had previously been noted in the *cyclo*pentadiene series would seem to be present also in other unsaturated cyclic systems, and may indeed be of much more frequent occurrence than is generally supposed.

Experimental.

The *iso*phorone employed was prepared by the condensation of mesityl oxide and ethyl acetoacetate (Knoevenagel and Fischer, *loc. cit.*), but at the temperature of the steam-bath for 4 hours, under which conditions the main portion of the *iso*phoronecarboxylic ester is converted into *iso*phorone. The fraction, b. p. 95—100°/14 mm., consisted of nearly pure *iso*phorone. In order to determine whether it was a single individual or a mixture of isomerides (compare Kerp and Muller, *loc. cit.*), its semicarbazone was submitted to a rigorous fractional crystallisation from alcohol. No trace of a second semicarbazone could be detected. The pure semicarbazone, crystallised from alcohol, has m. p. 199·5° (decomp.) (Crossley and

Gilling, *loc. cit.*, give 191°), and does not depress the melting point of a specimen prepared by the latter method (Found: C, 61·5; H, 8·8. Calc., C, 61·5; H, 8·8%). The ketone regenerated from the pure semicarbazone by steam distillation with oxalic acid had b. p. 99°/14 mm.; the oxime had m. p. 79·5° (Crossley and Gilling, *loc. cit.*, give 78°).

A *monopiperonylidene* derivative was obtained and after crystallisation from ethyl acetate had m. p. 145—146° (Found: C, 75·2; H, 7·0. $C_{17}H_{18}O_3$ requires C, 75·4; H, 6·7%).

Bromination of iso*Phorone*. *Formation of the Unstable Dibromide* (X).—A standard solution of dry bromine in dry carbon tetrachloride (1 c.c. = 0·1 g. Br) was added dropwise to a solution of 1 g. of dry *iso*phorone, in a little carbon tetrachloride cooled in ice, moisture being rigorously excluded. Decoloration was instantaneous, and when 2 c.c. had been added the crystalline dibromide began to separate. When 13 c.c. (1·3 g. Br) had been added, the solution became coloured with free bromine and a trace of hydrogen bromide could be detected. Addition of two atoms of bromine requires 1·2 g. of bromine. After traces of bromine and hydrogen bromide had been removed under diminished pressure, the product was broken into a large excess of water, and the liberated hydrobromic acid titrated with potassium hydroxide (Found: 0·56 g. of hydrogen bromide. Liberation of 1 mol. of hydrogen bromide requires 0·60 g.). In another experiment the solvent was removed by evaporation in a vacuum. The dibromide remained as a mass of short, thick prisms, m. p. about 40°, which on exposure to air immediately changed to a colourless oil with the evolution of hydrogen bromide.

Monobromoisophorone (XII).—The carbon tetrachloride solution of the unstable dibromide having been poured into water, the precipitated, colourless oil was extracted with pure ether and washed with very dilute alkali. The residue from the dried ethereal extract was left in an evacuated desiccator over potash for 24 hours, and since it could not be distilled without decomposition, was analysed in the crude state (Found: C, 50·4; H, 6·2. $C_9H_{18}OBr$ requires C, 49·8; H, 6·0%).

1 : 3 : 4 : 5(?)-*Tetrabromo*-3 : 3 : 5-*trimethyl*cyclo*hexan*-1-*one* is obtained by exhaustive bromination of *iso*phorone in carbon tetrachloride solution. After crystallisation from ethyl acetate–ligroin (b. p. 60—80°), it has m. p. 135° (Found: C, 24·0; H, 2·4; Br, 70·7. $C_9H_{12}OBr_4$ requires C, 23·7; H, 2·6; Br, 70·2%). The same compound is produced when an excess of bromine is added to *iso*phorone in ice-cold glacial acetic acid solution, and crystallises on keeping.

Attempts to prepare the tribromo-compound always resulted in the formation of an uncrystallisable gum.

Reduction of iso*Phorone.*—(1) *With sodium and moist ether. Formation of* 1 : 1′ : 3 : 3 : 3′ : 3′-*trimethyl*bicyclo*hexyl*-5 : 5′-*dione*, α and β forms (XVI and XVII). *iso*Phorone was dissolved in 20—30 times its volume of ether saturated with water, and sodium wire added in small successive portions. It seems to be essential to allow the first reaction to proceed as vigorously as possible. A flocculent solid separated, the liquid turning first yellow and finally deep red. The product was poured into water, acidified with hydrochloric acid, extracted with ether, and any acid fraction removed with sodium hydrogen carbonate solution. The neutral residue was a brown syrup which partly crystallised. The solid crystallised from ethyl acetate–ligroin had m. p. 162° (Found: C, 77·6; H, 10·8; *M*, cryoscopic in benzene, 268. $C_{18}H_{30}O_2$ requires C, 77·6; H, 10·8%; *M*, 280). It does not decolorise potassium permanganate in sodium hydrogen carbonate solution.

A *disemicarbazone* was obtained which after crystallisation from glacial acetic acid had m. p. 259—260° (decomp.) (Found: C, 61·0; H, 9·4. $C_{20}H_{36}O_2N_6$ requires C, 61·2; H, 9·3%).

The portion of the reduction product which had failed to solidify was fractionally distilled under reduced pressure. Low fractions consisting mainly of unchanged *iso*phorone were first obtained, and then a large, exceedingly viscous fraction distilled at 220—240°/20 mm., which immediately solidified when rubbed with low-boiling ligroin. The solid was crystallised from ethyl acetate–ligroin. It consists of the second isomeride, m. p. 126° (Found: C, 77·4; H, 10·7%). It does not decolorise potassium permanganate in sodium hydrogen carbonate solution in the cold, and only slowly on boiling. Careful fractional crystallisation of this substance failed to indicate the presence of any other product. A further quantity of this isomeride was obtained by a second fractional distillation of the gum obtained from the ligroin mother-liquors.

A *disemicarbazone* was obtained as before, but was precipitated from the alcoholic reaction mixture only on addition of water. After crystallising several times from about 90% methyl alcohol, it had m. p. 220° (decomp.) (Found: C, 61·2; H, 9·4%).

The same products were obtained when *iso*phorone was reduced with zinc and acetic acid, or with sodium amalgam and a boiling alkaline solution.

(2) *By the Clemmensen method. Formation of the hydrocarbon* (XIII). The ketone (10 g.) was refluxed with about 50 g. of amalgamated zinc and an excess of concentrated hydrochloric acid for 3 hours, small quantities of hydrochloric acid being occasionally

added. The reaction mixture was steam distilled. The first portion of the distillate consisted of a very small quantity of a volatile oil, with a camphoraceous odour, which was not obtained in quantity sufficient for identification. The hydrocarbon then distilled and solidified in the receiver, cooled in ice. The yield was small, a large amount of resinous material, non-volatile in steam, being produced. The hydrocarbon was extracted with ether, and the residue from the dried extract rapidly solidified. It crystallised from dilute alcohol in fine needles, m. p. 112° (Found: C, 88·5; H, 11·5; *M*, cryoscopic in benzene, 231. $C_{18}H_{28}$ requires C, 88·5; H, 11·5%; *M*, 244). It is stable to potassium permanganate in sodium hydrogen carbonate solution in the cold, but decolorises bromine in carbon tetrachloride solution, probably owing to the destruction of two of the bridge bonds.

Oxidation of the Hydrocarbon XIII.—The hydrocarbon (0·42 g.), suspended in a solution of potassium permanganate and sodium hydrogen carbonate, was heated under reflux, successive quantities of permanganate being added until the reaction mixture remained pink (48 hours). The product was steam-distilled to remove traces of the hydrocarbon, and the alkaline liquor was worked up in the usual manner, acidified at 0° with dilute sulphuric acid, and the product extracted with pure ether. The residue from the dried, ethereal extract immediately solidified. Crystallised from pure ether, it had m. p. 212—213°, either alone or mixed with a genuine specimen of *trans*-caronic acid (Found, by micro-combustion: C, 52·6; H, 6·7. Calc., C, 53·1; H, 6·4%). The oxidation was repeated, with the same result, on a fresh quantity of the hydrocarbon obtained by the reduction of a different specimen of *iso*phorone.

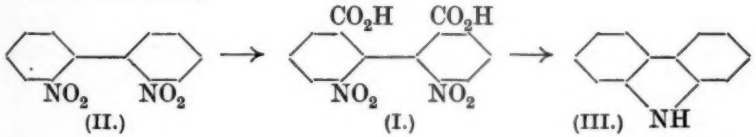
The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant with which the expenses of this research were met, and to Professor C. K. Ingold, F.R.S., for his continued interest and valuable suggestions during the progress of the investigation.

THE UNIVERSITY, LEEDS. [*Received, December 22nd*, 1925.]

XCIII.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VI. β-Dinitrodiphenic Acid; its Constitution and Resolution into Optically Active Components.*

By GEORGE HALLATT CHRISTIE, ALBERT HOLDERNESS, and JAMES KENNER.

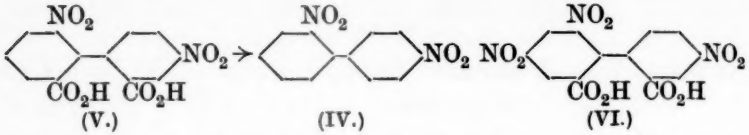
β-DINITRODIPHENIC acid, originally obtained by Schultz (*Annalen*, 1880, **203**, 108), is prepared by oxidation of the dinitroquinone produced, with its 2 : 7-isomeride, when phenanthraquinone is dinitrated. This acid has been regarded as a 6 : 6′-dinitrodiphenic acid (I) since it was examined by Schmidt and Kämpf (*Ber.*, 1903, **36**, 3745), who claimed to have converted it by distillation with dry sand into 2 : 2′-dinitrodiphenyl (II). "Wir erhielten dabei sehr wenig eines schwer löslichen Körpers vom Schelzpunkt ca. 240° (wahrscheinlich Dinitrofluorenon) und als Hauptproduct ca. 1 g. einer leichter löslichen Verbindung vom Schmelzpunkt 124—6° Dieselbe wurde genau verglichen mit o-o′-Dinitrodiphenyl, das wir uns nach den Angaben von Ullmann (*Ber.*, 1901, **34**, 3803) bereitet hatten. Beide Präparate zeigten in allen Eigenschaften völlige Uebereinstimmung."



(II.) (I.) (III.)

The conversion of the corresponding diaminodiphenic acid into carbazole (III) recorded at the same time supplied confirmatory, though obviously less conclusive, evidence in support of the very precise statement quoted, so that Kenner and Stubbings (J., 1921, **119**, 593) felt justified in regarding their synthetic 6 : 6′-dinitrodiphenic acid as a stereoisomeride of Schultz's acid when it was found that the two differed in properties.

The observations recorded by Christie and Kenner (this vol., p. 470) rendered it necessary, however, to re-examine Schultz's acid. The outcome of our experiments, carried out under somewhat different conditions from those used by Schmidt and Kämpf, was that in place of 2 : 2′-dinitrodiphenyl, m. p. 124°, 2 : 4′-dinitrodiphenyl (IV), m. p. 93°, was obtained, so that Schultz's acid would be 4 : 6′-dinitrodiphenic acid (V) :

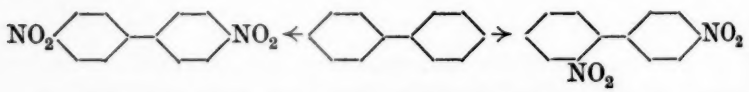


This result in itself is no more definite than that claimed by Schmidt and Kämpf, and perhaps somewhat less so if regard be paid to the considerably lower melting point of our product. Further, we were unable to detect any other product than 2 : 7-dinitrophenanthraquinone when 2-nitrophenanthraquinone was nitrated under the conditions for converting phenanthraquinone into 2 : 7- and what the above result would indicate to be 2 : 5-dinitrophenanthraquinones. The following considerations will, however, probably be held to be decisively in favour of our view rather than that of Schmidt and Kämpf :

(1) The same 2 : 4 : 7-trinitrophenanthraquinone is formed from the dinitroquinone in question and 2 : 7-dinitrophenanthraquinone, and attempts to prepare 2 : 4 : 5 : 7-tetranitrophenanthraquinone by further nitration have been unsuccessful (Christie and Kenner, *loc. cit.*).

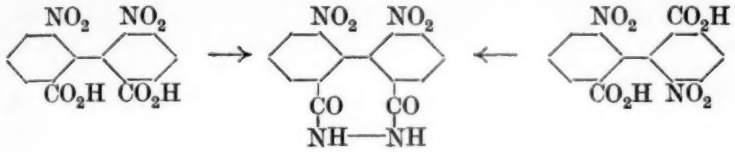
(2) It would be expected that if 4 : 5- and 2 : 7-dinitroquinones are produced from phenanthraquinone by nitration, some of the 2 : 5-isomeride also would be formed. But only two products have been observed.

(3) Dinitration of diphenyl furnishes the 2 : 4′- and 4 : 4′-derivatives as chief, if not sole products (Fittig, *Annalen*, 1862, **124**, 276) :



(4) The amino-group in 6-aminodiphenic acid is not diazotisable, but one of those in the diamino-acid, for which the 4 : 6′-constitution is now advocated, is diazotisable (Schmidt and Schall, *Ber.*, 1905, **38**, 3769). In previous papers, it was shown that such 6-amino-acids readily form phenanthridone derivatives. The accounts in the literature of the acids referred to make it not impossible that they may in reality be phenanthridone derivatives, as has been shown to be the case with other compounds similarly derived (compare Christie and Kenner, *loc. cit.*).

Kenner and Stubbings (*loc. cit.*) converted their synthetic 6 : 6′-dinitrodiphenic acid into a "hydrazide," and suggested that this derivative might furnish a means of converting the new acid into its supposed stereoisomeride :



This idea gained further credence when a "hydrazide" was prepared from the β-acid, and behaved similarly when heated. However, the "hydrazides" from the two sources differed in their behaviour towards acetic anhydride and were readily converted by oxidative hydrolysis with fuming nitric acid according to a procedure very briefly indicated by Curtius and Foersterling (*J. pr. Chem.*, 1895, **51**, 371), into acids melting, respectively, at 300° and 249—253°, as compared with 300° and 258—259° recorded for the original acids. Clearly, then, no interconversion of the acids is to be achieved through the hydrolysis of the "hydrazides" as intermediates.

β-Dinitrodiphenic acid, if it is the 4 : 6′-derivative, is closely related in constitution to 4 : 6 : 4′-trinitrodiphenic acid (VI), of which the resolution into optically active components through the agency of brucine has been described (Christie and Kenner, J., 1923, **123**, 779).

Similar experiments with the β-acid showed that it furnished a uniform brucine salt, but on the other hand two distinct quinine salts were obtained which were easily separable owing to their different solubilities in alcohol. From these salts, solutions of optically active acids and their sodium salts were prepared in the usual manner. A second illustration is therefore provided of an acid capable of existence in an asymmetric form when only three of the four 2, 6, 2′, and 6′-positions are occupied by substituents.

Since the stereoisomerism of β- and 6 : 6′-dinitrodiphenic acids, which originally inspired the experiments on their resolution, would now seem to be non-existent, it is perhaps desirable to record the fact that the resolution of the β-acid has been repeated with freshly prepared materials by Mr. V. M. Trikojus, B.Sc., in the laboratories of the University of Sydney.

Experimental.

β-Dinitrodiphenic acid, prepared by Schmidt and Kämpf's method (*loc. cit.*), was further characterised by the preparation of its *chloride*, colourless, rectangular plates, m. p. 120°, from benzene–light petroleum (Found : N, 7·9. $C_{14}H_6O_6N_2Cl_2$ requires N, 7·6%); its *ethyl* ester, colourless, pentagonal prisms, m. p. 114—115° (Found :

N, 7·3. $C_{18}H_{16}O_8N_2$ requires N, 7·2%); and its *amide*, colourless, hexagonal prisms, m. p. 247·5°, from dilute alcohol (Found: N, 17·2. $C_{14}H_{10}O_6N_4$ requires N, 16·9%).

Degradation of β-Dinitrodiphenic Acid to Dinitrodiphenyl.—A mixture of β-dinitrodiphenic acid with fine dry sand was distilled under the conditions described by Schmidt and Kämpf (*loc. cit.*); the yellow solid distillate, in agreement with their observation, melted at 240—245° after being extracted with alcohol, but the extract, which would have contained any dinitrodiphenyl which had been distilled, left practically no residue on distillation. The following modified procedure was therefore employed. A finely ground mixture of the acid (1 g.) with Naturkupfer C (0·1 g.) (compare Sabatier and Mailhe, *Compt. rend.*, 1914, **159**, 217) was distributed by stirring over sufficient glass wool to fill an Anschütz flask of 75 c.c. capacity. This flask was connected through a larger one to a filter-pump. When the mixture was very gradually heated in an oil-bath under a pressure of 30 mm., a reaction of explosive violence occurred at 285°. After the dense white vapours had subsided, both the distillate and the blackened residue were extracted with boiling alcohol. The extract was evaporated, diluted with water, and treated with cold dilute ammonia; a small solid residue was obtained. By solution in benzene of the product (0·45 g.) from eight such experiments, dark, insoluble matter was removed, and fairly homogeneous, transparent crystals closely resembling those of 2 : 4′-dinitrodiphenyl were obtained. After further purification by solution in light petroleum–benzene to remove a small quantity of less soluble, granular material, the product melted at 93°. A mixture with authentic 2 : 4′-dinitrodiphenyl melted at the same temperature, even after fusion and resolidification. A mixture with 2 : 2′-dinitrodiphenyl, m. p. 124°, shrank at 68—70°, was largely molten at 90°, but not completely so until 118°. After resolidification, the opaque mass commenced to clear at 90°, was almost all molten at 100—103°, and entirely liquid at 105°. The product was therefore 2 : 4′-dinitrodiphenyl.

For the preparation of the compound from diphenyl, light petroleum (b. p. 70—80°) was much more effective in the late stage of purification than the methyl alcohol recommended by Fittig (*Annalen*, 1862, **124**, 276).

Nitration of 2-Nitrophenanthraquinone.—After 2-nitrophenanthraquinone (10 g.) had been boiled under reflux with nitric acid (135 c.c.; *d* 1·5) and sulphuric acid (17 c.c.) for 30 minutes, the mixture was poured into water. From the solution of the precipitate in glacial acetic acid (1200 c.c.), 2 : 7-dinitrophenanthraquinone (8·9 g.), m. p. 301°, was deposited, whilst 0·4 g., m. p. 280—290°,

and 0·1 g., m. p. 225—293°, were recovered on concentrating the liquors to 200 c.c. and 50 c.c., respectively.

Hydrolysis of the "Hydrazides" of β- *and* 6 : 6′-*Dinitrodiphenic Acids.*—The "hydrazide" of β-dinitrodiphenic acid was prepared from the chloride in the manner already described for the corresponding derivative of 6 : 6′-dinitrodiphenic acid (Kenner and Stubbings, *loc. cit.*). It separates from acetone–light petroleum in small, colourless prisms, m. p. 294—295° (decomp.) (Found : N, 16·7. $C_{14}H_8O_6N_4$ requires N, 17·0%), and does not reduce Fehling's solution. Repeated but unsuccessful attempts were made to prepare a well-defined acetyl derivative of the "hydrazide" corresponding to that previously described as having been obtained from the "hydrazide" of 6 : 6′-dinitrodiphenic acid. The compound (0·25 g.) was heated with nitric acid (4 c.c.; *d* 1·5) for 75 minutes at 100°; the solution then deposited dinitrodiphenic acid, m. p. 300—301°, on dilution with water (15 c.c.).

The "hydrazide" of 6 : 6′-dinitrodiphenic acid was obtained in colourless prisms, m. p. 310° (decomp.), by crystallisation from acetone–light petroleum. The acid formed by hydrolysis with fuming nitric acid at 100° for 40 minutes was isolated by evaporation of the liquors at the ordinary temperature in an exhausted desiccator over sodium hydroxide. Its melting point, 249—253°, was not depressed when the acid was mixed with 6 : 6′-dinitrodiphenic acid.

Resolution of β-*Dinitrodiphenic Acid into Optically Active Components.*—A solution of the acid (2 g.) and hydrated brucine (5·61 g.) in boiling water (1050 c.c.) deposited, on cooling, fern-shaped sprays of irregular plates (3·9 g.), m. p. 209° (decomp.). By successive concentration to 575 c.c., 200 c.c., and 50 c.c., further crops of 2·2 g., m. p. 206° (decomp.), 0·3 g., m. p. 209° (decomp.), and 0·4 g., m. p. 207° (decomp.), were respectively obtained. The salt was hydrated [Found : H_2O, 4·2. $C_{60}H_{60}O_{16}N_6,2\frac{1}{2}H_2O$ requires H_2O, 3·9%. Found, for the salt dried at 130° : N, 7·8. $C_{12}H_6(NO_2)_2(CO_2H)_2,2C_{23}H_{26}O_4N_2$ requires N, 7·5%]. For 1·5% solutions in 10*N*-acetic acid of the anhydrous salt from each of the first two fractions, $[\alpha]_D = -13{\cdot}29°$ and $-13{\cdot}31°$, respectively. It was therefore not surprising that a solution of the sodium salt of the acid prepared from the brucine salt was inactive.

But when boiling solutions of the acid (4 g.) in alcohol (100 c.c.) and of quinine hydrate (9·2 g.) in alcohol (80 c.c.) were mixed, colourless, rectangular plates (5·7 g.), m. p. 178—179° (decomp.), separated on cooling; no further crystallisation occurred on concentration. On evaporating the alcohol, an oil remained, which was obtained in a solid condition by precipitation with light

petroleum from its solution in benzene. The melting point of the plates was unchanged after recrystallisation (Found: C_2H_6O, 2·45. $C_{54}H_{56}O_{12}N_6,\frac{1}{2}C_2H_6O$ requires C_2H_6O, 2·4. Found, for the salt dried at 130°: N, 8·6. $C_{54}H_{56}O_{12}N_6$ requires N, 8·6%). For a 1·43% solution of the dried salt in chloroform, $[\alpha]_D^{16°} = -218·1°$.

The more soluble salt melted at first at about 93°, but at 162—163° after being heated to constant weight at 120° (Found: N, 8·55. $C_{54}H_{56}O_{12}N_6$ requires N, 8·6%). For a 1·44% solution of the dried salt in chloroform, $[\alpha]_D^{16°} = -62·10°$.

d-β-*Dinitrodiphenic acid*, obtained from the less soluble quinine salt by treatment with hydrochloric acid, melted at 296°, whilst a mixture of the acid with the racemic acid melted over the range 285—293°.

For a 0·96% solution of the acid in ether, $[\alpha]_D^{14°} = +26·90°$, whilst for a 0·66% solution of the sodium salt in water, $[\alpha]_D^{15°} = -186·4°$.

l-β-*Dinitrodiphenic acid*, obtained from the more soluble quinine salt, also melted at 296°. For a 0·92% solution of the acid in ether, $[\alpha]_D^{15°} = -26·46°$, and for a 1·29% solution of the sodium salt in water, $[\alpha]_D^{15°} = +179·4°$.

Two of the authors (G. H. C. and A. H.) take this opportunity of expressing their gratitude to the Department of Scientific and Industrial Research for grants which enabled them to take part in this work. The authors are indebted to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials.

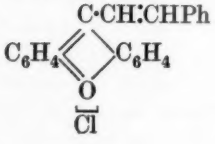
THE UNIVERSITY, SHEFFIELD. [*Received, December 28th*, 1925.]

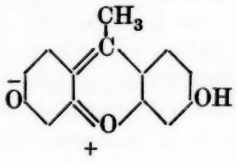
XCIV.—*Styrylpyrylium Salts. Part VI. Styryl Derivatives of 9-Methylxanthylium Chloride and 3 : 6-Dihydroxy-9-methylxanthylium Chloride.*

By HAROLD ATKINSON and ISIDOR MORRIS HEILBRON.

THE only styrylxanthylium salt recorded in the literature is 9-styrylxanthylium chloride (I), which Ziegler and Ochs (*Ber.*, 1922, **55**, 2257) obtained by the action of β-bromostyrene and

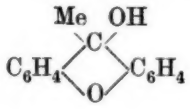
(I.)

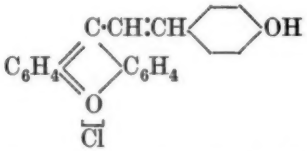




(II.)

magnesium upon xanthone. A more detailed study of styrylxanthylium salts has now been made in order to compare them with the members of the styrylbenzopyrylium series. As the method employed by Ziegler and Ochs could not readily be adopted for the preparation of salts containing substituents in either the styryl or the xanthylium residue, other methods of preparation had to be sought. The ease with which the anhydro-base, 6-hydroxy-9-methylfluorone (II), reacts with nitrous acid to form the *iso*-nitroso-derivative (Kehrmann, *Annalen*, 1910, **372**, 287) rendered it probable that a methyl group in position 9 in a xanthylium nucleus would show the same reactivity as an α- or γ-methyl group does in the benzopyrylium series. In order to test this point, an attempt was made to prepare 9-methylxanthylium chloride which had previously been prepared by Decker (*Ber.*, 1905, **38**, 2493) in the form of its double ferrichloride salt by the action of magnesium methyl iodide upon xanthone. The free chloride can actually be isolated, but it is difficult to obtain in good yield. On the other hand, an ethereal solution of the easily accessible 9-methylxanthenol (III) may be utilised in place of the chloride itself. Thus, on saturation of the solution mixed with benzaldehyde with dry hydrogen chloride, 9-styrylxanthylium chloride, identical in all respects with the compound prepared by Ziegler and Ochs (*loc. cit.*), was readily obtained. Similar condensations have been

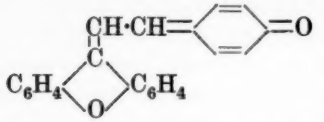
(III.) 

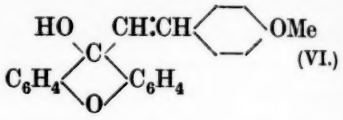

(IV.)

effected with *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde, piperonal, and vanillin, and in all cases excellent yields obtained.

The styrylxanthylium salts containing substituents in the styryl residue are highly coloured, crystalline compounds, readily soluble in formic acid, giving deep red to purple solutions. In their reaction towards water and alkali, they behave similarly to the unsubstituted 2-styrylbenzopyryliums (Buck and Heilbron, J., 1922, **121**, 1198). Thus, when 4′-hydroxy-9-styrylxanthylium chloride (IV) was dissolved in dilute formic acid, a reddish-violet solution resulted which on dilution with a large excess of water slowly changed to blue. This colour effect we attribute, as in former cases, to formation of the quinonoid anhydro-base (V), for with 4′-methoxy-9-styrylxanthylium chloride, where such isomerisation is precluded, the solution rapidly becomes opalescent and decolorised, followed by deposition of the colourless carbinol base (VI).

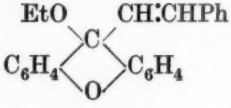
3′ : 4′-Methylenedioxy-9-styrylxanthylium chloride, which dissolves in formic acid with a blue colour, reacts similarly. The same effect

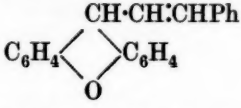
(V.) 

(VI.) 

is noted on treatment of the formic acid solutions with dilute sodium hydroxide. On the other hand, with the 4′-hydroxy-derivatives the quinonoid anhydro-bases are first precipitated and then slowly isomerise to the colourless carbinol bases (compare Dilthey and Taucher, *Ber.*, 1920, **53**, 252). In all cases, the effect of heat on the colourless carbinol solutions produces a reversion in colour, a fact indicating that at higher temperatures the oxonium bases are more stable than the isomeric carbinol compounds. This phenomenon has also been observed by Bunzly and Decker (*Ber.*, 1904, **37**, 2931) in the case of 9-phenylxanthenol.

The behaviour of these styrylxanthylium chlorides towards alcohol is peculiar. Ziegler and Ochs (*loc. cit.*) noted that on trituration of 9-styrylxanthylium chloride with alcohol, 9-styryl-xanthyl ethyl ether (VII) was formed, while, on the other hand, boiling with this solvent produced 9-styrylxanthen (VIII). A

(VII.) 


(VIII.)

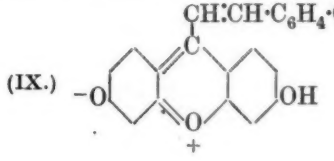
preliminary study of the styrylxanthylium chlorides containing substituents in the styryl residue has shown that when these are kept in contact with small quantities of alcohol, they are gradually converted into colourless substances, all of which crystallise from acetone in well-defined crystals with sharp melting point. The compounds thus prepared have been analysed, but in each case the carbon content is too high for formulation either as an ethyl ether, xanthen or allene derivative. The formation of the last type of compound from other styryl derivatives was noted by Meyer and Schuster (*Ber.*, 1922, **55**, 815), and Ziegler and Ochs, by boiling 9-styrylxanthenol with glacial acetic acid, obtained a compound the composition of which would agree with that of an allene derivative. A full investigation of these interesting compounds is at present being undertaken.

Walker and Heilbron (J., 1925, **127**, 685) have shown that in the γ-styrylbenzopyryliums the presence of a free hydroxyl group in the meta-position to pyrylium oxygen inhibits the change to quinonoid anhydro-base on water dilution. In order to ascertain

whether a similar effect holds in this series, styrylxanthylium salts prepared from 3 : 6-dihydroxy-9-methylxanthylium chloride have been examined. The latter compound, which has been described by Kehrmann (*loc. cit.*), can be isolated directly in good yield by continuously passing dry hydrogen chloride into a molten mixture of resacetophenone and resorcinol until the mass solidifies.

3 : 6-*Dihydroxy-9-styrylxanthylium Salts.*—The general method employed was to saturate with dry hydrogen chloride a suspension of 3 : 6-dihydroxy-9-methylxanthylium chloride in alcohol containing a slight excess of the required aldehyde. Condensation usually started in the cold and was completed by boiling under reflux; the suspended chloride then gradually disappeared and the condensation product separated either from the boiling solution or on cooling. These salts differ from those having the unsubstituted xanthylium nucleus in being soluble in alcohol without change, whilst the colour of the solutions both in this solvent and in formic acid is considerably lighter. A notable point is that whereas 3 : 6-dihydroxy-9-methylxanthylium chloride is characterised by its strong fluorescence in alkaline solution, substitution of the styryl radical for the methyl group caused the complete disappearance of this property. The colour changes observed on dilution with water or treatment with alkali differ essentially from those of the unsubstituted styrylxanthylium members. A neutral alcoholic solution of 3 : 4′ : 6-trihydroxy-9-styrylxanthylium chloride remains unaltered on dilution, and in presence of alkali the orange-red colour only changes to bright red, due doubtless to salt formation. 3 : 6-Dihydroxy-4′-methoxy-9-styrylxanthylium chloride reacts similarly, for neither on dilution nor in presence of alkali does isomerisation to the carbinol base occur. The non-formation of this can only be attributed to the presence of the hydroxyl groups, which stabilise the molecule, presumably by formation of the betaine (IX). The same phenomenon must consequently hold for the 4′-hydroxy-analogue, but apart from this no structural change from benzenoid to quinonoid can be assumed.

(IX.)



EXPERIMENTAL.

9-*Methylxanthylium chloride* was prepared by a modification of Decker's method (*loc. cit.*). Xanthen (30 g.) was dissolved in

boiling benzene (250 c.c.), and the Grignard reagent (12 g. of magnesium and 66 g. of methyl iodide) gradually added. The solution immediately became orange and a yellow solid separated. This was rapidly reabsorbed, however, and later a colourless. crystalline compound separated from the greyish-green liquid. The whole was boiled under reflux for 1 hour, after which the ether and about half the benzene were removed. The solid was filtered off from the cold solution, washed with dry ether, and decomposed with cold water. The yellow solution so formed was repeatedly extracted with ether until the aqueous layer gave only a pale yellow colour on the addition of concentrated hydrochloric acid. After drying over sodium sulphate, this ethereal solution was employed directly for the preparation of the styryl salts. In order to obtain 9-methylxanthylium chloride, the solution was saturated with dry hydrogen chloride; the colour then changed from pale yellow to green and on standing in the ice-chest, dark red crystals separated. After recrystallisation from a mixture of anhydrous formic acid and ether containing hydrogen chloride, the salt was obtained in golden needles, m. p. 175°, and identified by means of the double ferrichloride, m. p. 204°, and mercurichloride (compare Decker, *loc. cit.*). The melting point of the ferrichloride is given in the literature as 240°, but this is possibly a typographical error.

9-*Styrylxanthylium Chlorides*.—The general method of preparation of these salts consisted in the addition of the aldehyde in slight excess to the dry ethereal solution of 9-methylxanthenol, the mixture being then saturated with dry hydrogen chloride, when condensation readily took place. The actual amount of xanthenol in solution was not ascertained, but the Grignard reaction, by means of which it was prepared, was assumed to have given a quantitative yield.

9-*Styrylxanthylium chloride* rapidly separated from the condensation mixture of 9-methylxanthenol and benzaldehyde either as golden, glistening plates or as red needles with a bright green sheen. The plates melted at 95°, the same melting point as that given by Ziegler and Ochs (*loc. cit.*), but the red needles melted over a range of temperature (66—92°) and probably contained some easily lost addenda. This salt was proved to be identical with that prepared by Ziegler and Ochs by means of the deep red double salt with zinc chloride (m. p. 188°) and its ethyl ether (m. p. 168—169°).

4′-*Hydroxy*-9-*styrylxanthylium chloride*. On passing dry hydrogen chloride into the well-dried ethereal solution of 9-methylxanthenol and excess of *p*-hydroxybenzaldehyde, the solution gradually passed

through orange to dark red and a violet oil with bronze reflex separated. The mixture having been left in the ice-chest for several hours, the ether was poured off; the oil gradually solidified to a green, amorphous mass. This was taken up in a small amount of warm anhydrous formic acid previously saturated with hydrogen chloride, and dry ether was added to the cold filtered solution in small quantities at a time; the styryl salt then separated in long, bright-green, lustrous needles containing 1 mol. HCO_2H. These were immediately transferred to a large test-tube, which was then evacuated, whereby adherent hydrogen chloride was removed and the crystals were rendered stable. If this was not done, the compound tended to become resinous, a tendency exhibited by all members of this series. The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving dark violet solutions. It was sparingly soluble in cold chloroform to a blue solution which changed to reddish-brown on warming but reverted to blue on cooling. The same colour change on heating was shown by a solution in nitrobenzene. When a large volume of water was added to a very dilute formic acid solution (wine-red colour), no immediate change of colour occurred, but on standing (6 hours) the solution became pure blue. The addition of water to a more concentrated formic acid solution caused the immediate separation of a violet, amorphous precipitate, presumably the anhydro-base (V) (Found: C, 69·4; H, 4·5; Cl, 9·4. $C_{22}H_{17}O_4Cl,HCO_2H$ requires C, 69·4; H, 4·5; Cl, 9·3%). In contact with absolute alcohol, the salt was partly converted into a colourless, crystalline substance, but this change was not absolutely complete despite repeated trituration, even after 15 days. The substance crystallises from acetone in long, colourless needles, m. p. 228° (Found: C, 85·0; H, 5·8%).

4′-*Methoxy*-9-*styrylxanthylium chloride* separated from the condensation liquor in dark green crystals. Considerable difficulty was experienced in obtaining it in a stable crystalline state sufficiently pure for analysis, but this was ultimately accomplished by crystallisation from chloroform containing hydrogen chloride; it then separated in bright green needles, m. p. 98°, which were rendered stable by removal of all addenda in a vacuum. The salt dissolved readily in formic and glacial acetic acids, giving dark violet solutions. When a dilute solution in formic acid was treated with water, a strong opalescence immediately developed, the wine-red colour rapidly faded, and the colourless carbinol base was deposited. As with the 4′-hydroxystyryl salt, long trituration with alcohol gave a colourless compound, m. p. 194°, of undetermined constitution. The *ferrichloride*, prepared by the action of powdered hydrated ferric

chloride on a solution of 4′-methoxy-9-styrylxanthylium chloride in formic acid, separated from glacial acetic acid in long, copper-coloured plates which softened and turned blue at 175° and decomposed with inflation at 212° (Found : C, 51·5; H, 3·2; Cl, 27·7; Fe, 10·5. $C_{22}H_{17}O_2Cl_4Fe$ requires C, 51·7; H, 3·3; Cl, 27·8; Fe, 10·9%).

4′-Hydroxy-3′-methoxy-9-styrylxanthylium chloride crystallised from formic acid in golden-brown needles which contained a molecule of formic acid (m. p. 135°). The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving royal-blue solutions. Neutralisation of a dilute formic acid solution with sodium carbonate precipitated the colour base, which was gradually converted into the colourless carbinol base (Found : C, 67·1; H, 4·6; Cl, 8·9. $C_{22}H_{17}O_3Cl,HCO_2H$ requires C, 67·2; H, 4·6; Cl, 8·7%).

3′ : 4′-Methylenedioxy-9-styrylxanthylium chloride could not be obtained pure, for although it separated from the condensation mixture in green crystals, attempts to recrystallise these from either formic acid or glacial acetic acid with or without the addition of hydrogen chloride resulted in the formation of a yellow oil, which gradually solidified to a colourless compound. Recourse was made, therefore, to analysis of the *zinc chloride* double salt, which was readily prepared by suspending the crude xanthylium chloride in cold formic acid and shaking vigorously with zinc chloride in hydrochloric acid. The salt separated from glacial acetic acid in glistening, green needles (Found : C, 49·6; H, 3·1; Cl, 20·3. $C_{22}H_{15}O_3Cl_3Zn,H_2O$ requires C, 51·2; H, 3·3; Cl, 20·6%).

3 : 6-Dihydroxy-9-methylxanthylium Chloride.—Dry hydrogen chloride was passed into a molten mixture of resacetophenone (10 g.) and resorcinol (7·2 g.) (oil-bath at 140—150°). The melt gradually turned red and, after several hours, became semi-solid. The stream of hydrogen chloride was continued until the mass became too viscous, the temperature being gradually raised to 170°. The solid mass was dissolved in boiling anhydrous formic acid (80 c.c.); the xanthylium chloride then separated in reddish-yellow needles with a characteristic blue metallic reflex. On several occasions, however, the salt was deposited as a chocolate powder, which was again recrystallised from formic acid containing hydrogen chloride. It is soluble in alcohol, acetone, or formic acid and insoluble in ether or benzene. It dissolves in sodium hydroxide solution to a reddish-brown solution which when dilute shows an intense green fluorescence. With sodium acetate it yields the base in the form of brick-red flocks.

3 : 4′ : 6-Trihydroxy-9-styrylxanthylium Chloride.—The parent

chloride (5 g.) was suspended in 70 c.c. of alcohol together with *p*-hydroxybenzaldehyde (2·6 g.), and dry hydrogen chloride was passed into the cold solution; the xanthylium chloride then gradually dissolved. After ½ hour the styrylxanthylium chloride (4·3 g.) separated from the deep red solution as a red, amorphous solid. On recrystallisation from anhydrous formic acid containing hydrogen chloride, it formed long needles which appeared red by transmitted and green by reflected light. On heating the chloride changed to red and melted with inflation at 273—274°. It is readily soluble in hot formic acid, sparingly soluble in alcohol or acetone to orange-red solutions, whilst in dilute sodium hydroxide it dissolves, giving a permanent bright claret-red solution (Found: C, 65·1; H, 4·2; Cl, 9·0. $C_{21}H_{15}O_4Cl,H_2O$ requires C, 65·5; H, 4·4; Cl, 9·2%).

3 : 6-*Dihydroxy*-4′-*methoxy*-9-*styrylxanthylium chloride* separated as a dark red, amorphous solid (70% yield) on passing hydrogen chloride into a boiling alcoholic suspension of equimolecular quantities of the parent chloride and anisaldehyde. It was purified by boiling with alcohol, which removed any uncondensed products, and was then crystallised from formic acid containing hydrogen chloride. It forms golden-coloured plates with a metallic sheen which on heating change to green and melt at 282° (decomp.). It is very sparingly soluble in boiling alcohol or acetone, but readily soluble in hot formic acid. It dissolves in warm dilute sodium carbonate to a bright red solution, from which the base separates on cooling (Found: C, 65·9; H, 4·6; Cl, 8·7. $C_{22}H_{17}O_4Cl,H_2O$ requires C, 66·2; H, 4·8; Cl, 8·9%).

3 : 4′ : 6-*Trihydroxy*-5′-*methoxy*-9-*styrylxanthylium chloride* crystallises from formic acid in reddish-violet needles which appear green by reflected light (m. p. 244—245°). It is readily soluble in alcohol, acetone, or hot formic acid and dissolves in dilute sodium hydroxide solution with a deep reddish-violet colour. It is extremely hygroscopic and specimens were dried at 100° immediately prior to analysis (Found: C, 66·6; H, 4·4; Cl, 8·8. $C_{22}H_{17}O_5Cl$ requires C, 66·6; H, 4·3; Cl, 8·9%).

3 : 6-*Dihydroxy*-4′ : 5′-*methylenedioxy*-9-*styrylxanthylium chloride* separates from formic acid containing hydrogen chloride in bronze-coloured needles which, on heating, turn green and decompose at 316°. It is very sparingly soluble in alcohol, but dissolves readily in boiling formic acid to a red solution (Found, in material heated at 80° for several hours: C, 66·8; H, 3·9; Cl, 9·3. $C_{22}H_{15}O_5Cl$ requires C, 66·9; H, 3·8; Cl, 9·0%).

3 : 6-*Dihydroxy*-4′-*dimethylamino*-9-*styrylxanthylium Chloride*.—A suspension of the parent chloride (5 g.) and *p*-dimethylamino-

benzaldehyde (3·2 g.) in 100 c.c. of alcohol was boiled for 10 minutes under reflux without addition of hydrogen chloride, the condensation product separating as a hard, green solid. On recrystallisation from a large volume of alcohol, it formed microscopic, green needles which on heating changed to red. It is sparingly soluble in alcohol or acetone, giving intense green solutions which change to claret-red on dilution with water. Addition of hydrochloric acid to the alcoholic solution produces a yellow solution of the xanthylium chloride hydrochloride. The salt dissolves in aqueous sodium hydroxide to a bright scarlet solution, which is not altered on further dilution (Found: C, 66·6; H, 5·2; Cl, 8·8. $C_{23}H_{20}O_3NCl,H_2O$ requires C, 67·1; H, 5·3; Cl, 8·6%).

We wish to record our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (H. A.) which enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, December 28th*, 1925.]

XCV.—*Arylsulphuric Acids.*

By GEORGE NORMAN BURKHARDT and ARTHUR LAPWORTH.

THE use of dialkylanilines in place of pyridine for the preparation of arylsulphuric acids by Verley's method [*Bull. Soc. chim.*, 1901, **25**, 46; compare Durand and Huguenin, Brit. Pat. 186057 (1922), 202630 and 202632 (1923)] has been found to lead to rather better yields and recovery of tertiary base is simplified.

Diethylaniline (100 g.; 2½ mols.) or the equivalent quantity of dimethylaniline in carbon disulphide (100 c.c.) was stirred mechanically and cooled to −10°. Chlorosulphonic acid (34 g.; 1·1 mols.) was run in steadily during 15 minutes, the temperature being maintained below 10°. Phenol (25 g.; 1 mol.) in carbon disulphide (50 c.c.) was then added all at once, the mixture stirred for an hour, and the disulphide thereafter removed by distillation on a steam-bath. The cold, viscous residue was run into a solution of sodium hydroxide (22 g.) in water (150 c.c.) containing 10 g. of hydrated barium hydroxide,* with vigorous shaking, the temperature being kept below 35°. A large proportion of the diethylaniline could

* For certain purposes, the use of excess of ammonia instead of the hydroxide of an alkali metal is advantageous; but in this case, before removing the tertiary base in a current of steam, it is necessary to add sufficient barium hydroxide to convert all salts present into barium salts, as ammonium phenyl sulphate may suffer hydrolysis in the steam distillation process.

then be separated directly and the remainder removed by steam distillation or by extraction with benzene; the aqueous residue on direct evaporation yielded 90% of the theoretical quantity of sodium phenyl sulphate together with 7% of sodium chloride.

If the base and phenol were mixed before the chlorosulphonic acid was added, the yields never exceeded 60% of the theoretical.

Use of Sulphuric Anhydride in place of Chlorosulphonic Acid.—The authors carried out a number of experiments on the use of sulphuric anhydride in place of the chlorosulphonic acid employed by Verley (*loc. cit.*), as the formation of hydrogen chloride in the preparation is often disadvantageous. The experiments were completed before the patents of Durand and Huguenin (Brit. Pat. 202632 of 1923) came to their notice, but some of the observations made were not redundant and appear worthy of record.

As it was evident that the use of sulphuric anhydride as sulphating agent for phenols would render it easy to isolate pure products, trials of a number of organic media as solvents were made. The liquids were cooled and the anhydride was distilled slowly into them. Chloroform and carbon tetrachloride were decomposed rapidly, yielding carbonyl chloride even with most careful cooling, and carbon disulphide evolved carbonyl sulphide. Diethylaniline could not be made to dissolve the anhydride without charring and sulphonation; hexane did not appear to dissolve the anhydride as such, but was rapidly attacked when in contact with it: the nature of the reaction in the latter instance is under investigation. Experiments in which sulphuric anhydride was distilled into a cooled solution containing both phenol and diethylaniline in carbon tetrachloride gave more promising results, but even in presence of the tertiary base about 13% of the anhydride was destroyed by reaction with the tetrachloride, and the mixed salts obtained at the end of the operation contained 8% of inorganic chloride.

The only solvent found to dissolve sulphuric anhydride readily and without decomposition was liquid sulphur dioxide, and the following is an account of one of the experiments in which it was tried as solvent for sulphating phenols.

A solution of sulphuric anhydride (19 g.) in 80 c.c. of liquid sulphur dioxide was slowly added with vigorous stirring to phenol (20 g.) and diethylaniline (60 g.) in a wide-mouthed flask, cooled in a freezing mixture. After remaining over-night to allow most of the solvent to evaporate, it was found that much of the latter was obstinately retained and had to be removed by heating for an hour on a steam-bath. The product, after cooling, was neutralised with aqueous sodium hydroxide and sufficient barium hydroxide to precipitate inorganic sulphate. Nearly pure sodium phenyl

sulphate in 60% yield was isolated on removal of diethylaniline and evaporation of the aqueous residue.

Use of Pyridine Sulphuro-anhydride in the Preparation of Salts of Phenylsulphuric Acids. [With FRANK ASHWORTH].—This method is virtually a modification of the process last described, inasmuch as sulphuric anhydride with a tertiary base, in this instance pyridine, is used. The following is an example of its application to a nitrophenol.

Sulphur trioxide (25 g.) is slowly distilled, with stirring and drastic cooling, into pyridine (29 g.; 1·75 mols.). Benzene (200 c.c.) is now added, and the whole heated to boiling * under a reflux condenser. *p*-Nitrophenol (30 g.; 1 mol.) is next introduced and the whole boiled for 4 hours, during which time the pyridine salt of *p*-nitrophenylsulphuric acid crystallises out. The mixture is cooled, poured into a slight excess of aqueous potassium hydroxide, the benzene distilled off under diminished pressure, the residual solution made just acid with acetic acid, and unchanged nitrophenol (2 g.) extracted with ether. The solution is rendered slightly alkaline once more and the water and pyridine evaporated off under diminished pressure, when potassium *p*-nitrophenyl sulphate is obtained in yields of 90—94% of the theoretical.

Eugenol under similar conditions gave a 70% yield of potassium eugenyl sulphate.

o-Nitrophenol proved much more difficult to attack than the para-isomeride. Yields of the sulphate up to 25% were obtained when equivalent proportions of *o*-nitrophenol and pyridine sulphuro-anhydride were used, and 56% yields with twice the theoretical amount of the latter.

Use of Pyrosulphate and Tertiary Bases in the Preparation of Phenylsulphuric Acids.—It is somewhat remarkable that there are no published records of attempts to extend or improve upon the results obtained by Baumann (*Ber.*, 1878, **11**, 1907), who succeeded in making potassium phenyl sulphate from phenol by means of potassium pyrosulphate. He worked with aqueous solutions only, however, with potassium hydroxide as condensing agent, and the yields were very poor. The present authors have found that good yields of the phenyl sulphates can be obtained by heating finely powdered potassium pyrosulphate with a solution of the phenol or naphthol in dry dimethylaniline, followed by extraction of the product with aqueous alkali.

A mixture of phenol (1 mol.) and dimethyl- or diethyl-aniline (1 mol.) was heated on a steam-bath and stirred mechanically while

* Control experiments showed that pyridine sulphuro-anhydride has no appreciable action on boiling benzene.

finely powdered potassium pyrosulphate * (1½ mols.) was added; the suspension was stirred and heated for 8 hours. The reaction mixture was poured into a suspension of excess of baryta in cold water, the base being subsequently removed by steam distillation, the excess of baryta being precipitated by means of carbon dioxide. After filtering and evaporating, potassium phenyl sulphate in 80—85% yield was easily isolated.

Another experiment using phenol (1 mol.), base (3 mols.), and pyrosulphate (2½ mols.), heated and stirred for 4 hours, gave a yield of 90%.

The method was also found satisfactory for α- and β-naphthols, and for eugenol and *iso*eugenol, except that in all these cases it was impossible to use barium hydroxide on account of the low solubility of the salts of the products. A slight excess of potassium hydroxide was therefore added and the base separated while the solution was hot.

Notes on the Properties of the Salts of Arylsulphuric Acids.—Baumann and Verley (*loc. cit.*) recorded (*a*) that the potassium salts of the arylsulphuric acids are stable to alkalis, but are readily hydrolysed by acids; (*b*) that they decompose, with some isomerisation to sulphonates, at 150—200°; (*c*) one or two physical properties in a few instances. Heymann and Koenigs oxidised potassium *o*- and *p*-tolyl sulphates to the corresponding carboxylic acids (*Ber.*, 1886, **19**, 704). In the present investigation many of the above observations were confirmed and extended, and a variety of salts of arylsulphuric acids examined in some detail.

The salts show some variations in their ease of hydrolysis. The alkali salts are stable at 100° in neutral aqueous solution and require heating to boiling before rapid hydrolysis sets in in presence of mineral acid. The barium salt is decomposed on heating to 100° in aqueous solution for 1½ hours, after which the hydrolysis proceeds rapidly to completion in 2 hours. The ammonium and magnesium salts are of intermediate stability. All the salts are stable at 100° in an aqueous solution of sodium acetate even in presence of a considerable concentration of acetic acid. Hydrolysis of the potassium salt is also brought about by heating at 150° with strong alkali or with half-concentrated ammonia at 190—220° for 4 hours. In the latter case, no aniline is produced.

* Potassium pyrosulphate was made by heating powdered potassium hydrogen sulphate, under 2—3 mm. pressure, in a bolthead flask on a sand-bath. The reaction proceeded at 270—330° and was stopped when the temperature began to rise rapidly. The mass was then poured on to an iron plate and allowed to cool in a desiccator; it contained 90% of pyrosulphate. The salt was powdered and sieved as rapidly as possible immediately before application in the above reactions, otherwise it deteriorated.

Heating with aniline gave no indication of replacement of the hydroxyl group. Diazo-compounds do not couple to an appreciable extent with salts of phenylsulphuric acid in alkaline solution, and nitrous acid is without action, even after several days. Concentrated nitric acid rapidly decomposes the alkali salts, producing a mixture of nitro-derivatives without tarring or much evolution of heat. The bromination of salts of phenylsulphuric acids is described in another communication. Potassium phenyl sulphate crystallises in anhydrous, rhombohedral or six-sided plates with apex angle 95°. It dissolves to the extent of 0·7% in alcohol and 14% in water at 17°, and is freely soluble in both media when hot (Found: K, 18·3. Calc. for $C_6H_5O_4SK$, K, 18·5%).

The sodium salt forms rhombic plates consisting of aggregates of twinned leaflets. It dissolves to the extent of 7% in alcohol and 31% in water at 17°, and is freely soluble in both media when hot (Found: Na, 9·3. Calc. for $C_6H_5O_4SNa,3H_2O$, Na, 9·2%). The barium salt forms fine granules and is rather less readily soluble in water than is barium chloride; in hot or cold alcohol, it dissolves to the extent of about 15%; when the moist salt is exposed in a steam-oven it is quantitatively decomposed in a few minutes, phenol being liberated, and the same change occurs at the ordinary temperature in the course of a few days. The ammonium salt is extremely soluble in cold water and crystallises in hydrated, rhombohedra composed of thin plates like the sodium salt. The magnesium salt forms small, nacreous, rectangular or six-sided plates; it is less soluble in cold water than any of the other salts examined.

Salts of the isomeric tolylsulphuric acids are very sparingly soluble in cold alcohol and acetone and only slightly soluble in hot; they can be recrystallised from 85% alcohol, and, in the case of the *p*-tolyl derivative, from acetone containing 2% of water. They are very freely soluble in acetone containing 5% of water. The *o*-salt is soluble to the extent of 22% in water at 17°, the *m*- 9%, and the *p*- 10%.

p-*Toluidine tolyl sulphates* are characteristic. They were prepared as follows: Potassium tolyl sulphate (5·5 g.) was added to a hot solution of *p*-toluidine (2 g.) in 50 c.c. of alcohol, the mixture stirred for a minute with the liquid just below the boiling point, and *p*-toluidine hydrochloride (3·5 g.) added. The solution was boiled and shaken for a few minutes, and the potassium chloride (1·8 g.) which separated was filtered off. On evaporation, the liquor gave an almost theoretical yield of the toluidine tolyl sulphate, which was washed with benzene and recrystallised from benzene containing 5% of alcohol. The salts from *o*- and *p*-cresols are fairly soluble in

water and readily in alcohol and acetone but insoluble in benzene. On recrystallisation, they formed matted, woolly needles which on melting or heating for some time at 110° gave *p*-toluidine sulphate and free cresol. The salt from *o*-cresol melted sharply with decomposition at 125—127°, and the *p*-salt at 149—151°.

Potassium m-*carboxyphenyl sulphate* was prepared by oxidation of the *m*-tolylsulphate. The latter (30 g.) was dissolved in water (100 c.c.) containing a little potassium hydroxide. A hot saturated solution of potassium permanganate (60 g.) was added to the solution, and the mixture heated on the steam-bath for 8 hours, after which the excess permanganate was reduced by means of alcohol, and the precipitate removed by filtration. The filtrate after cooling was rendered slightly acid with hydrochloric acid. The flocculent precipitate formed was collected, washed, and recrystallised from 70% alcohol. The yield was 80%. The salt forms plates: 3·2 parts dissolve in 100 parts of water at 17°; it is readily soluble in acetone containing 10% of water (Found: K, 15·3. $C_7H_5O_6SK$ requires K, 15·3%). It gave no coloration with ferric chloride. It was hydrolysed, on boiling with mineral acid, yielding *m*-hydroxybenzoic acid and potassium hydrogen sulphate.

Salts of Naphthylsulphuric Acids.—These are readily obtained in yields of 80—90% by the methods described on pp. 684 and 686. High purity of the naphthols is important in using the latter method or the products are discoloured.

Potassium α-*naphthyl sulphate* crystallises from water as a coarse, crystalline powder or in long, soft needles. It dissolves in 40 parts of water at 17°, is freely soluble in hot water, and almost insoluble in most of the usual organic media (Found: K, 14·7. $C_{10}H_7O_4SK$ requires K, 14·9%).

Potassium β-*naphthyl sulphate* resembles its isomeride in general appearance and characters, but its crystals are hydrated. It dissolves in 70 parts of water at 17° (Found: K, 11·9. $C_{10}H_7O_4SK,4H_2O$ requires K, 11·7%).

Both these salts are stable to boiling alkalis and to boiling dilute acetic acid in presence of sodium acetate; they are easily hydrolysed, however, by hot dilute mineral acids. They are at once attacked in aqueous solution by bromine, and precipitates soluble in ether are formed together with free sulphuric acid; the elimination of the sulphate residue is not, however, complete after several minutes in presence of excess of bromine.

A considerable amount of time was spent in investigating the oxidation of the isomeric potassium naphthyl sulphates with alkaline permanganate in aqueous solution. It was found that rapid oxidation took place at 80°, and from the quantity of free

inorganic sulphate formed, that about 42% of the α-salt underwent oxidation in the unsubstituted ring, and in the case of the β-isomeride about 62%. Numerous attempts to separate from the resulting mixtures the sulphates of the hydroxyphthalic, hydroxyphthalonic acids, or the corresponding products formed after elimination of the sulphate radicals were not successful, owing mainly to the excessive solubility of these acids and their derivatives.

From potassium α-naphthyl sulphate, a small amount of the hydroxyphthalic acid (m. p. 150°) and some phthalic acid were obtained (compare Miller, *Annalen*, 1881, **208**, 247).

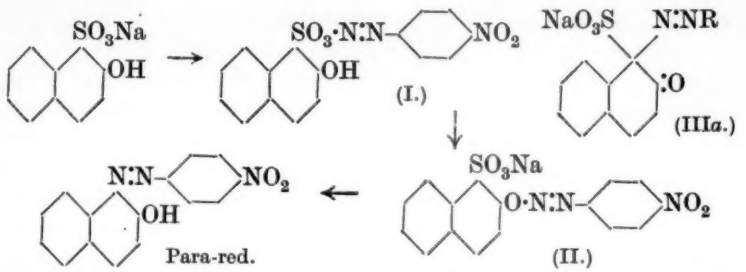
The authors wish to acknowledge a grant from the Research Fund of the Chemical Society towards the expenses of this investigation, and a maintenance grant to one of them (G. N. B.) from the Department of Scientific and Industrial Research which enabled him to take part in the later sections of the work.

THE UNIVERSITY, MANCHESTER. [*Received, December 28th*, 1925.]

XCVI.—*A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part I. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from 4′-Nitrobenzene-2-naphthol-1-diazosulphonate.*

By FREDERICK MAURICE ROWE, ESTHER LEVIN, ALAN CHAMLEY BURNS, JOHN STANLEY HERBERT DAVIES, and WOLFE TEPPER.

SOME β-naphtholsulphonic acids condense with diazo-compounds in acid solution to form stable diazosulphonates; thus, β-naphthol-1-sulphonic acid or oxy-Tobias acid (Bayer & Co., Brit. Pat. 11757 of 1895) gives diazosulphonates which Grant Hepburn (Brit. Pat. 116360) found to possess interesting properties. For example, Para-red is obtained in substance quantitatively by dissolving one molecular proportion of 4′-nitrobenzene-2-naphthol-1-diazosulphonate in an aqueous solution of sodium carbonate or of one molecular proportion of sodium hydroxide, and then acidifying the cold solution. Diazosulphonates derived from β-naphthol-1-sulphonic acid appear to be the only examples in which the stabilising component can provide subsequently an azo-coupling component. Bucherer (*Ber.*, 1909, **42**, 47; "Lehrbuch der Farbenchemie," 1914, 125), without giving experimental details, explains this reaction thus:



Wahl and Lantz (*Bull. Soc. chim.*, 1923, **33**, 97) have re-examined the above reaction and agree with Bucherer's conclusion that compound (II) is a diazo-oxide, but were unable to isolate an analogous compound from 1-bromo-(or chloro)-β-naphthol, although the latter reacts with diazotised *p*-nitroaniline to form Para-red as shown by Hewitt and Mitchell (J., 1906, **89**, 1169).

As Wahl and Lantz state that they propose to study the diazo-oxides which can be prepared from β-naphthol-1-sulphonic acid and other diazo-compounds, we must mention here that we began our present investigation in 1918 with an examination of these compounds. Diazosulphonates derived from β-naphthol-1-sulphonic acid are stable, whereas the compounds formed from them by the action of one molecular proportion of alkali are unstable and particularly sensitive to acids. If the latter are diazo-oxides, it is not clear why they should be more reactive and unstable than diazosulphonates, and, in view of our other results, we suggest that they are sodium aryl-1-azo-β-naphthaquinone-1-sulphonates of the general formula (III*a*). Compounds of this type would be hydrolysed readily by cold dilute acid, forming azo-β-naphthol derivatives. It might be anticipated that such compounds would give different reduction products from those obtained from corresponding diazo-oxides, but they are so unstable that the reduction products more probably would be derived from the corresponding azo-β-naphthol derivative, owing to the preliminary elimination of the sulphonic group. In support of this, we find that even the more stable diazosulphonates give 1-amino-2-naphthol on reduction.

Grant Hepburn (*loc. cit.*) observed that although Para-red is obtained by acidifying a solution of 4′-nitrobenzene-2-naphthol-1-diazosulphonate in one molecular proportion of aqueous sodium hydroxide, this is not the case if an excess of sodium hydroxide is used, and he handed over the investigation of this interesting reaction to one of us (F. M. R.).

When the orange solution of 4′-nitrobenzene-2-naphthol-1-diazosulphonate in aqueous sodium carbonate is added to an excess of cold aqueous sodium hydroxide, or vice versa, the temperature

rises and a crimson colour is developed immediately, which changes slowly to orange-brown, or more rapidly when warmed on the water-bath. There is no evolution of nitrogen, and no formation of sodium β-naphthol-1-sulphonate or sodium *p*-nitrophenylnitrosoamine. Subsequent acidification gives traces only of Para-red, and, consequently, a reaction has occurred in which the whole of the diazosulphonate has taken part. No organic by-products can be detected and a homogeneous yellow compound can now be isolated in excellent yield.

In order to test the generality of this reaction, various diazosulphonates were prepared, using other diazo-compounds in place of diazotised *p*-nitroaniline. Each diazosulphonate was converted by sodium carbonate into a sodium aryl-1-azo-β-naphthaquinone-1-sulphonate, many of which were isolated in a well-crystalline condition, and all of which were converted quantitatively into the corresponding azo-derivative of β-naphthol, with elimination of the sulphonic group, by the action of cold dilute acid. On the other hand, only certain diazosulphonates give rise to the new reaction with sodium hydroxide. For example, the compounds from aniline, *o*- and *p*-toluidine, 2 : 5-dichloroaniline, tribromoaniline, sulphanilic acid, *p*-aminoacetanilide, anthranilic acid, *p*-aminobenzonitrile, α- and β-naphthylamine, and benzidine are decomposed by sodium hydroxide with formation of sodium β-naphthol-1-sulphonate and evolution of nitrogen or formation of the nitrosoamine, although the reaction was examined under a variety of conditions. On the other hand, the compounds, for example, from *o*- and *m*-nitroaniline, 2 : 4-dinitroaniline, 4-nitroaniline-2-sulphonic acid, 4-chloro-2-nitroaniline, 4-nitro-2-chloroaniline, 2 : 6-dibromo-4-nitroaniline, and 3-nitro-4-aminotoluene give rise to the new reaction with sodium hydroxide, accompanied usually by the development of a transient intense colour, and new compounds are formed with properties similar to those of the compound derived from *p*-nitroaniline. In fact, the only compounds which have yet been found to give rise to the new reaction, and which do not contain a nitro-group, are aminoazo-compounds, such as 4-aminoazobenzene and its sulphonic acid. The suitability of a diazo-compound for participation in the new reaction depends mainly on the formation of a condensation product with β-naphthol-1-sulphonic acid, sufficiently stable to react further with sodium hydroxide without decomposition.

The possibility of using other compounds in place of β-naphthol-1-sulphonic acid was examined next. Diazotised *p*-nitroaniline condenses with β-naphthylamine-1-sulphonic acid, but the product does not react in the new way, nor is there any evidence of the

occurrence of the new reaction with β-naphthol-8-sulphonic acid or phenol-*o*-sulphonic acid. Naphthalene-α-sulphonic acid condenses with diazotised *p*-nitroaniline (Becker, D.R.-P. 89998) and the diazosulphonate dissolves in aqueous sodium carbonate, but the addition of sodium hydroxide to the solution causes decomposition with formation of sodium naphthalene-α-sulphonate and sodium *p*-nitrophenylnitrosoamine. Consequently, the presence of a hydroxyl group in the *o*-position with respect to the sulphonic group in the naphthalene nucleus is an essential feature of the new reaction. 1-Methyl-β-naphthol condenses with diazotised *p*-nitroaniline and its *o*-sulphonic acid, probably with formation of diazo-oxides, but these also are decomposed by sodium hydroxide. Finally, there was no evidence of the occurrence of the new reaction when diazotised *p*-nitroaniline and 1-bromo-β-naphthol were used, for the halogen atom in the latter compound is so labile that Para-red is produced under all conditions. Consequently, β-naphthol-1-sulphonic acid stands alone in giving rise to the new reaction.

From this point our attention has been confined to a detailed study of the compound formed by the action of an excess of sodium hydroxide on a solution of 4′-nitrobenzene-2-naphthol-1-diazosulphonate in aqueous sodium carbonate.

This compound has the formula $C_{16}H_{12}O_7N_3SNa$ and is the sodium salt of a sulphonic acid. Aqueous solutions are decolorised by zinc dust and ammonia, and are reoxidised to a deeper colour, indicating, *inter alia*, that a nitro-group has been reduced to an amino-group. Reduction proceeds further with hydrosulphite [hyposulphite] or acid stannous chloride, and, although concordant results were obtained with difficulty in titrations with titanous chloride or sulphate, the figures indicated that 8 atoms of hydrogen were required for complete reduction as compared with 6 for the mere reduction of a nitro- to an amino-group. When an aqueous solution of the compound $C_{16}H_{12}O_7N_3SNa$ is boiled with aqueous mineral acid, the sulphur is eliminated as sulphur dioxide, thus:

$$R{\cdot}SO_3H + H_2O = R{\cdot}OH + SO_2 + H_2O.$$

This behaviour is not confined to this compound, but is a common property of all the analogous compounds which we have yet prepared, and gave the first clue to the actual mechanism of the new reaction, for although the sulphonic group in β-naphthol-1-sulphonic acid is hydrolysed by similar treatment, β-naphthol is formed and not 1 : 2-dihydroxynaphthalene. The hydroxy-derivative has the formula $C_{16}H_{13}O_5N_3$ and with alkaline hydrosulphite a compound $C_{16}H_{17}O_3N_3$ is formed as the sole reduction product, *i.e.*, not only

has a nitro-group been reduced to an amino-group, but an additional two hydrogen atoms have been introduced. Reduction with acid stannous chloride, alone or in presence of granulated tin, however, gave varying results according to the duration and temperature of the reaction, and two further compounds were obtained. Closer investigation showed that whether alkaline hydrosulphite or acid stannous chloride is used, the initial reduction product is the compound $C_{16}H_{17}O_3N_3$. The latter, however, reacts with boiling hydrochloric acid, forming the compound $C_{14}H_{11}ON_3$, which is capable of undergoing further change with acid-reducing agents, forming the compound $C_{14}H_{12}ON_2$. Thus, although several derivatives and degradation products were obtained, we failed to bring about fission into two aromatic products by these reactions.

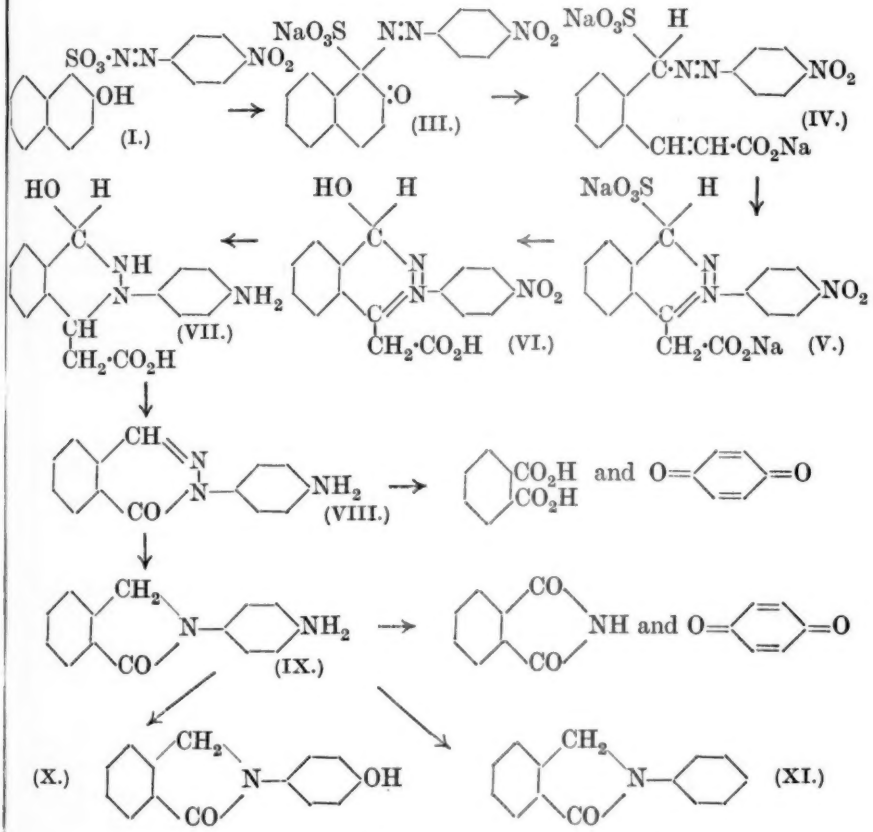
We wish to acknowledge here our great indebtedness to Professor Arthur Lapworth, F.R.S., and to Professor Robert Robinson, F.R.S., who first propounded the explanation of the mechanism of the new reaction upon which our constitutional formulæ are based, and to whom our warmest thanks are due for their interest in this investigation.

The course of the reaction in the case of 4′-nitrobenzene-2-naphthol-1-diazosulphonate (I) is outlined in the scheme on p. 695.

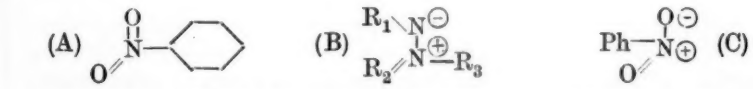
Reference has been made already to the compounds formed by the action of aqueous sodium carbonate on diazosulphonates derived from β-naphthol-1-sulphonic acid, and regarded hitherto as diazo-oxides. It would not be anticipated that diazo-oxides would react with alkali hydroxides in the manner outlined on p. 695, and it is upon the occurrence of this new reaction and the properties of the compounds to which it leads, that our opinion is based that the former compounds are really *sodium aryl*-1-*azo*-β-*naphthaquinone*-1-*sulphonates*. It is considered that sodium hydroxide opens the ring * of *sodium* 4′-*nitrobenzene*-1-*azo*-β-*naphthaquinone*-1-*sulphonate* (III) with addition of sodium hydroxide, forming the intermediate carboxylic acid (IV), which is not isolated, and a quinonoid modification of which would account for the transient intense coloration. The next step is a rearrangement and closing of the ring which we believe occurs as shown in (V) with formation of *disodium* 3-(4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetate*-1-*sulphonate*, and when the mixture is rendered faintly acid, the *monosodium* salt separates. The replacement of the sodium-1-sulphon-

* The opening of the naphthalene ring forming a carboxylic acid has also been effected by Werner and Piguet (*Ber.*, 1904, **37**, 4310), who prepared *o*-cyanocinnamic acid by the very vigorous reaction which occurs when a pyridine solution of 1-nitroso-β-naphthol is treated with benzenesulphonyl chloride or sulphuryl chloride.

ate group by hydroxyl gives 1-*hydroxy*-3-(4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* (VI). Formula (VI) is in agreement with the behaviour of this compound on reduction, whereby 1-*hydroxy*-3-(4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic acid* (VII) is formed.



N.B.—Formulæ (V) and (VI) above correspond with the familiar formula for nitrobenzene (A), but the formulæ may be expressed equally well as containing the semi-polar bond (B), corresponding with the form (C) for nitrobenzene.



Attempts to degrade compound (VI) by oxidation with acid dichromate were unsuccessful and gave an apparently more com-

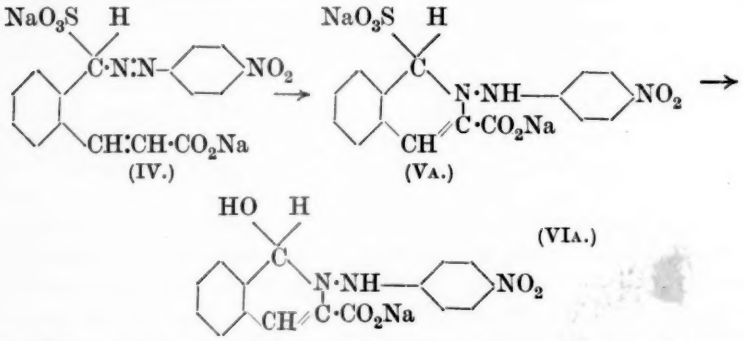
plex compound, which has been set aside for future investigation, as has also a compound formed by boiling with aqueous sulphuric acid.

The oxidation of compound (VII) with acid dichromate proceeded satisfactorily only if limited, and the compound formed has also been set aside for future investigation.

When compound (VII) is boiled with aqueous mineral acid, it is converted into 4′-*amino*-3-*phenylphthalaz*-4-*one* (VIII), the latter constitution being supported by the fact that oxidation with hot acid dichromate gives phthalic acid and benzoquinone.

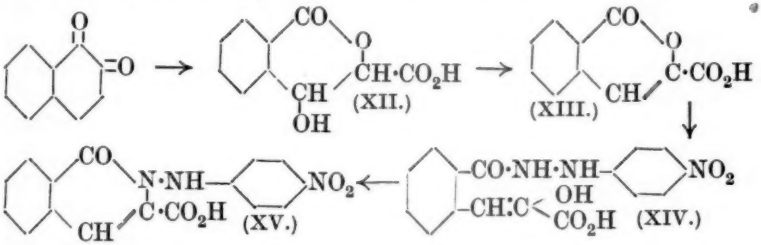
When compound (VIII) is reduced with zinc dust and hydrochloric acid, one nitrogen atom is eliminated as ammonia and 4′-*amino*-N-*phenylphthalimidine* (IX) is produced. Thus, this reaction is similar to that observed by Racine (*Annalen*, 1887, **239**, 78) in the preparation of *N*-phenylphthalimidine (XI) from 3-phenylphthalaz-4-one by reduction with tin and hydrochloric acid. The constitution of compound (IX) was confirmed by the preparation from it of *N*-phenylphthalimidine (XI), and also by oxidation with cold acid dichromate, when phthalimide and benzoquinone were obtained. The fact that phthalimide was obtained in this case suggests that it was also the primary oxidation product of compound (VIII), but that hydrolysis then occurred at the temperature necessary for satisfactory oxidation in the latter case.

At an early stage in our investigation it appeared possible that the rearrangement and closing of the ring in passing from compound (IV) might occur with the formation of *N*-arylimino-derivatives of *iso*quinoline thus :



In order to determine which of the two schemes for the final stage in the reaction is correct, the compound (VI) or (VIA) was studied closely. It might be argued that a compound such as (VIA) would give *p*-phenylenediamine as one of its reduction products, whereas we failed to obtain any trace of *p*-phenylenediamine by the reduc-

tion of this compound. As the literature appeared to contain no reference to *N*-arylimino-derivatives of *iso*quinoline, for purposes of comparison with compound (VI) or (VIA), a related compound undoubtedly of the type of the latter was synthesised thus :



β-Naphthaquinone was oxidised by calcium hypochlorite (Zincke and Scharfenberg, *Ber.*, 1892, **25**, 399; compare Zincke, *ibid.*, 1168, 1493; Bamberger and Kitschelt, *ibid.*, 888) to the δ-lactone of *o*-carboxyphenylglyceric acid (XII), and this was converted into *iso*coumarin-3-carboxylic acid (XIII) by heating with hydrochloric acid at 160—165°. It was anticipated that the latter would condense with *p*-nitrophenylhydrazine in alcoholic solution with elimination of water, forming N-4′-*nitrophenylimino*iso*carbostyril*-3-*carboxylic acid* (XV), as Bamberger and Frew (*Ber.*, 1894, **27**, 198) prepared *N*-phenyl*iso*carbostyril-3-carboxylic acid in this way, using aniline. Actually, this condensation gave in our case the *hydrazide* (XIV), and the final stage of the synthesis was completed only by boiling a suspension of the latter in toluene in presence of phosphorus trichloride.

Compound (VI) or (VIA) dissolves in alkalis with a deep wine-red colour, and is reduced by hydrosulphite to compound (VII) in almost theoretical yield. Compound (XV) dissolves in alkalis with a deep red colour, but when reduced with hydrosulphite under exactly the same conditions, although no *p*-phenylenediamine could be detected and the sole reduction product was an *amino-acid*, the yield of the latter was much inferior to that obtained in the former case. This is probably due to the fact that compound (XV) is much more sensitive to alkalis than compound (VI) or (VIA). Other noteworthy differences between the properties of the two compounds were observed. Thus, whereas compound (VI) or (VIA) is esterified readily by passing hydrogen chloride through a solution in the requisite alcohol, or by means of the alcohol and sulphuric acid, or by the action of alkyl halides on the silver salt, we failed to esterify the carboxyl group in compound (XV). Further, compound (VI) or (VIA) forms an *anilide* when boiled with aniline in toluene solution in presence of phosphorus trichloride, but

compound (XV) is unaffected by this treatment. These differences in the properties of the two carboxylic acids are probably due to the proximity of the imino- and carboxyl-groups in compound (XV), and indicate the improbability of formula (VIA), particularly as we failed to prepare a nitroso-derivative of the compound, or to detect an imino-group in it by alkylation. In order to arrive at a definite conclusion on this point, the behaviour of compound (VI) or (VIA), when heated with an excess of zinc dust, was examined next, as Bamberger and Frew (*loc. cit.*) found that *N*-phenyl*iso*carbostyril-3-carboxylic acid gives *iso*quinoline when treated in this manner. In our case, however, we failed to obtain any trace of *iso*quinoline, a fact which appeared definitely to exclude formula (VIA). This is supported also by the fact that one of our later degradation products (VIII) undoubtedly contains two nitrogen atoms in the ring, and it is difficult to conceive how such a compound could be formed from an *iso*quinoline derivative. Further support of formula (VI) is afforded by the fact that when this compound is heated carefully above its melting point, nitrobenzene is formed, together with a basic residue which has not yet been examined closely; this behaviour is analogous to that of *p*-nitroazoxybenzene, which also gives nitrobenzene and a basic residue under similar conditions.

Consequently, formulæ (VA) and (VIA) have been discarded and it appears that formulæ (V) and (VI) are correct, although the possibility of tautomeric forms of these, such, for example, as (VIB), $C_6H_4<\begin{matrix}C(OH):N\\ CH\text{—}N\cdot C_6H_4\cdot NO_2\\ CH_2\cdot CO_2H\end{matrix}$, must not be overlooked. This is virtually an *iso*amide of a carboxylic acid, however, and it is improbable that such a compound would be reduced by alkaline hydrosulphite in the manner shown in (VII).

In the present state of our investigation, formulæ (V) and (VI) appear the most probable and agree best with the formulæ assigned to their derivatives and degradation products which we have yet prepared, although it is possible that the former may require slight modification in the light of future work. The closing of the ring which occurs in passing from (IV) to (V) is a condensation of a type closely allied to the condensation of nitrosobenzene and ethyl methylenemalonate recently described by Burkhardt and Lapworth (J. 1925, **127**, 1749).

Noteworthy features of the new reaction described in this communication are the simplicity and neatness with which certain naphthalene derivatives are converted into complex phthalazine derivatives. The latter by simple means are capable of almost

quantitative conversion into many other interesting compounds, which are now rendered readily accessible for further study.

Further work on this subject is in progress and the investigation will be extended in the various directions indicated.

EXPERIMENTAL.

Monosodium 3-(4′-*Nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid*-1-*sulphonate* (compare V).—A filtered solution of 48 g. of commercial sodium β-naphthol-1-sulphonate in 220 c.c. of water was stirred into a cold solution of diazotised *p*-nitroaniline, obtained by adding a concentrated solution of 14 g. of sodium nitrite to a solution of 24 g. of *p*-nitroaniline in 60 c.c. of concentrated hydrochloric acid and 240 c.c. of water. The 4′-nitrobenzene-2-naphthol-1-diazosulphonate (I) separated immediately as an orange precipitate in theoretical yield (calculated on the *p*-nitroaniline). This was filtered, washed free from acid with brine, made into a paste with 150 c.c. of cold water, and stirred into a cold solution of 48 g. of anhydrous sodium carbonate in 120 c.c. of water. A solution was produced but, if kept, crystals of *sodium* 4′-*nitrobenzene*-1-*azo*-β-*naphthaquinone*-1-*sulphonate* (III) separated. The cold orange solution was added immediately to a cold solution of 40 g. of sodium hydroxide in 80 c.c. of water, the temperature rose about 15°, and the deep crimson mixture was left overnight until the colour had changed completely to yellowish-brown. It was rendered faintly acid with hydrochloric acid, then made alkaline with sodium carbonate, and a trace of Para-red filtered off. The filtrate was rendered faintly acid with hydrochloric acid and, under these conditions, the product separated completely as a yellow, semi-crystalline precipitate. (N.B.—Many experiments were carried out to determine the best conditions for the preparation of this compound, and although the yield was not affected materially, variations of temperature, excess of sodium hydroxide, and duration of the reaction, gave a resinous product which coagulated slowly.) After drying, sodium chloride was removed by extraction with absolute alcohol, from which solvent the product crystallised in orange, prismatic needles (yield 66 g.; 91·5% of the theoretical) (Found : C, 46·3; H, 2·9; N, 10·4; S, 7·5; Na, 5·2. $C_{16}H_{12}O_7N_3SNa$ requires C, 46·5; H, 2·9; N, 10·2; S, 7·7; Na, 5·5%). It is readily soluble in water, but less soluble in alcohol, forming yellow solutions, which are deepened by the addition of alkalis. The aqueous solution is decolorised by zinc dust and ammonia, and on exposure to air a deeper colour returns. It is a level-dyeing, pure greenish-yellow acid dye of good tinctorial power and of good fastness to other influences, but fugitive to light, even when dyed

in admixture with a fast blue. When heated with concentrated nitric acid at 105° in a sealed tube for 8 hours, decomposition occurs and picric acid was isolated in yellow needles, m. p. 122°.

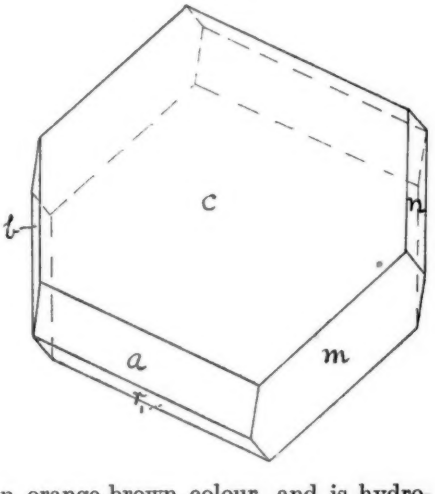
1-*Hydroxy*-3-(4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid* (VI).—A solution of 32 g. of monosodium 3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid 1-sulphonate in 120 c.c. of water was boiled with 64 c.c. of concentrated hydrochloric acid (aqueous sulphuric acid also can be used) until evolution of sulphur dioxide had ceased, and the product, which separated first as an oil, had formed yellowish-brown crystals. The latter were washed with boiling water and crystallised from ethyl acetate in pale yellow, vitreous, irregular prisms, m. p. 241° (yield 24 g.; 94%). Sulphur dioxide evolved during the reaction was determined quantitatively in the usual manner and was equivalent to one molecular proportion (Found : C, 58·9; H, 4·2; N, 12·8. $C_{16}H_{13}O_5N_3$ requires C, 58·7; H, 4·0; N, 12·8%). When the substance was heated carefully above its melting point, nitrobenzene (confirmed by conversion into aniline) was obtained, together with a basic residue which has not yet been examined closely. This behaviour is analogous to that of *p*-nitroazoxybenzene, which also gives nitrobenzene under similar conditions. The substance is readily soluble in alcohol, acetone, or glacial acetic acid, but less soluble in benzene or ether. It is sparingly soluble in water, forming a solution acid to litmus, but dissolves readily in sodium carbonate or hydroxide with a deep wine-red colour, and prolonged boiling of the alkaline solution causes decomposition. It forms a reddish-brown *silver* salt and a yellowish-brown *barium* salt, and decolorises bromine water. It dissolves in cold concentrated sulphuric acid with an orange colour and is reprecipitated unaltered on dilution, but when 5 g. were dissolved in 50 c.c. of sulphuric acid, then diluted with 60 c.c. of water, and the solution boiled under reflux for 1 hour, there was no precipitate on further dilution. A substance (4 g.) was isolated and crystallised from alcohol in fine yellow needles, m. p. 331°, but this has not yet been examined closely.

Derivatives of 1-*Hydroxy*-3-(4′-*nitrophenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic Acid.*—*Methyl ester.* A solution of 5 g. in 50 c.c. of dry methyl alcohol was saturated with dry hydrogen chloride at 0°, left over-night, and then boiled under reflux for 2 hours. The *ester* crystallised from methyl alcohol in yellow prisms, m. p. 153° (Found : C, 59·8; H, 4·6; N, 12·5. $C_{17}H_{15}O_5N_3$ requires C, 59·8; H, 4·4; N, 12·3%). *Ethyl ester.* (*a*) A solution of 3 g. in 30 c.c. of dry ethyl alcohol was boiled with 1·5 g. of concentrated sulphuric acid under reflux for 4 hours. (*b*) The dry, reddish-brown, amorph-

ous silver salt, precipitated by the addition of silver nitrate to a neutral solution of 5 g. in sodium hydroxide, was boiled with 2 g. of ethyl iodide and 50 c.c. of dry ethyl alcohol under reflux for 1 hour. (*c*) As described above for the methyl ester, except that 60 c.c. of dry ethyl alcohol were used. The three products were identical in all respects and crystallised from ethyl alcohol in yellow crystals, tabular in character and with hexagonal outline; m. p. 180°. We have been furnished with the following crystallographic description of the substance by Mr. H. E. Buckley of the Department of Crystallography, University of Manchester, to whom we express our grateful thanks :

" The symmetry is anorthic (triclinic) pinacoidal, with $a : b : c = 1{\cdot}387 : 1 : 0{\cdot}626$ and $\alpha = 78° 15'$, $\beta = 40° 10'$, $\gamma = 117° 6'$.

FIG. 1.



The forms usually developed are *a*(100), *b*(010), *c*(001), tabular, *n*(011) and *r*($\bar{1}$01) (Fig. 1).

Angles measured: $a : b = 118° 11'$, $a : c = 39° 42'$, $a : m = 54° 53'$, $c : m = 56° 42'$, $c : n = 57° 53'$, $c : b = 103° 19'$, $n : r = 68° 19'$, $m : n = 35° 45'$, and $c : r = 89° 10'$ " (Found : C, 61·1; H, 4·7; N, 12·1. $C_{18}H_{17}O_5N_3$ requires C, 60·8; H, 4·8; N, 11·8%). It dissolves in sodium carbonate with an orange-brown colour, and is hydrolysed to the original acid by boiling with alcoholic potassium hydroxide. Attempts to acetylate the ester gave a yellow, resinous product which could not be crystallised. *Acetyl derivative.* A solution of 5 g. of the acid in 10 c.c. of glacial acetic acid was boiled with 5 c.c. of acetic anhydride under reflux for 8 hours, and then poured on to ice. The *acetyl* derivative crystallised from ethyl alcohol in greenish-yellow, vitreous prisms, m. p. 212° (Found : C, 58·8; H, 4·2; N, 11·7. $C_{18}H_{15}O_6N_3$ requires C, 58·5; H, 4·1; N, 11·4%). It dissolves in sodium carbonate with an orange-brown colour or in sodium hydroxide with a wine-red colour, and attempts to esterify it gave resinous products which could not be crystallised. *Anilide.* A fine suspension of 4 g. of the acid in 400 c.c. of toluene was boiled with 2·3 g. of aniline and 1 g. of

phosphorus trichloride under reflux for 5 hours with stirring. When cold, the residue was washed with a little sodium carbonate and, after several crystallisations from ethyl acetate, formed yellow needles, m. p. 190—192° (decomp.) (Found : C, 65·4; H, 4·6; N, 13·9. $C_{22}H_{18}O_4N_4$ requires C, 65·7; H, 4·5; N, 13·9%). The anilide dissolves in sodium hydroxide with a red colour and is hydrolysed to the original acid by boiling concentrated hydrochloric acid. *Oxidation of* (VI). A fine suspension, obtained by dissolving 20 g. in 200 c.c. of cold concentrated sulphuric acid and pouring on to 800 g. of ice, was oxidised by adding gradually 10 g. of powdered sodium dichromate. Next day the product was precipitated completely by nearly neutralising with sodium hydroxide and, after several crystallisations from ethyl alcohol and ethyl acetate, yellow leaflets (11·5 g.), m. p. 247°, were obtained, but this substance requires further investigation.

1-*Hydroxy*-3-(4′-*aminophenyl*)-*tetrahydrophthalazine*-4-*acetic Acid* (VII).—Hydrosulphite was added to a solution of 12 g. of 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 150 c.c. of water and 10 g. of sodium hydroxide at about 90° until the deep wine-red colour had disappeared, the mixture being kept alkaline throughout by the addition of sodium hydroxide. The yellow solution was filtered and, if the filtrate was cooled, fine yellow needles of the *sodium* salt separated incompletely. The product was best isolated, therefore, by the addition of hydrochloric acid until a white precipitate had separated completely. The end-point is readily determined, because too much acid redissolves the precipitate with a brown colour. It was washed with cold water and crystallised from a large volume of boiling water in colourless prisms, m. p. 239° (yield 10·7 g.; 97·5%) (Found : C, 64·3; H, 5·7; N, 14·2. $C_{16}H_{17}O_3N_3$ requires C, 64·2; H, 5·7; N, 14·0%). This compound can also be obtained by rapid reduction with acid stannous chloride, but the yield is not so good owing to the subsequent action of acid upon it. It is soluble in alcohol, insoluble in benzene, and gives a transient wine-red colour with ferric chloride. It dissolves readily in dilute alkalis or dilute acids and can be diazotised. The esters could not be obtained by the reduction of the esters of 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid with alkaline hydrosulphite, for hydrolysis also occurred, nor did direct esterification prove satisfactory. The fact that the compound is affected by acids interfered with the preparation of a pure *acetyl* derivative, for, after crystallisation from dilute acetic acid, colourless plates, softening at 145—165° and melting sharply at 266°, were obtained (Found : C, 64·3; H, 5·2; N, 12·3. $C_{18}H_{19}O_4N_3$ requires C, 63·3; H, 5·6;

N, 12·3%). *Oxidation of* (VII). Powdered sodium dichromate (7 g.) was added in small portions during 3 hours to a solution of 20 g. in 400 c.c. of water and 100 c.c. of concentrated sulphuric acid at the air temperature. A transient wine-red colour was produced after each addition, but any further addition did not produce this colour. The mixture was rendered just alkaline with sodium hydroxide, diluted with water to 2 litres, boiled, filtered, the filtrate neutralised, and concentrated. After crystallisation from alcohol and then from water, yellow, prismatic needles (15 g.), m. p. 276°, were obtained, but this substance requires further investigation.

4′-*Amino*-3-*phenylphthalaz*-4-*one* (VIII).—A solution of 12 g. of 1-hydroxy-3-(4′-aminophenyl)-tetrahydrophthalazine-4-acetic acid in 300 c.c. of concentrated hydrochloric acid (25—30% aqueous sulphuric acid also can be used) was boiled under reflux. A less soluble *hydrochloride* separated progressively in colourless needles after 1 hour and the reaction was completed by boiling for 18 hours. After cooling, the hydrochloride was filtered off and converted into the base, which crystallised from alcohol in deep straw-coloured, prismatic needles, m. p. 259° (yield 8·8 g.; 92·5%) (Found: C, 71·0; H, 4·7; N, 17·8. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·6; N, 17·7%). It is soluble in hot water, insoluble in alkalis, but soluble in dilute acids and can be diazotised, although we have not yet succeeded in removing the amino-group or replacing it by a hydroxyl group without the compound undergoing further change. *Acetyl derivative.* A solution of 1 g. in 10 c.c. of glacial acetic acid was boiled with 0·5 c.c. of acetic anhydride. After a few minutes the colourless acetyl derivative separated completely; it crystallised from a large volume of boiling water in almost colourless plates, m. p. 348° (Found: C, 68·9; H, 4·8; N, 14·9. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%). *Oxidation of* (VIII). A solution of 5 g. in 400 c.c. of water and 80 c.c. of concentrated sulphuric acid was oxidised at the air temperature by adding gradually 16 g. of powdered sodium dichromate. A brown precipitate separated and next day benzoquinone, yellow needles, m. p. 115°, was isolated by extraction with ether. The other oxidation product could not be obtained satisfactorily under these conditions, but was obtained in a second oxidation in which a further 14 g. of dichromate were added and the mixture heated. In this case extraction with ether gave phthalic acid, colourless needles, m. p. 197° (confirmed by conversion into phthalic anhydride, colourless needles, m. p. 129°, and by the formation of fluorescein).

4′-*Amino*-N-*phenylphthalimidine* (IX).—A solution of 20 g. of 4′-amino-3-phenylphthalaz-4-one in 1 litre of water and 100 c.c. of

concentrated hydrochloric acid was boiled, and 300 c.c. of concentrated hydrochloric acid were added, followed by 30 g. of zinc dust in small portions during 2½ hours with vigorous boiling so that the volume was reduced to 700 c.c. After cooling, the product separated completely as colourless plates of the *hydrochloride*, together with a small proportion of colourless needles of the *zinc double chloride*. Completion of the reaction was indicated by the pink colour of the filtrate, and the latter contained ammonia. The crystals were dissolved in a little hot water and hydrochloric acid, the solution was rendered alkaline, and the dry precipitate extracted with alcohol. The base crystallised in almost colourless, prismatic needles, m. p. 198° (yield 16·5 g.; 87%) (Found: C, 75·1; H, 5·5; N, 12·4. $C_{14}H_{12}ON_2$ requires C, 75·0; H, 5·4; N, 12·5%). *Acetyl derivative*. A solution of 1 g. in 10 c.c. of glacial acetic acid was boiled with 0·5 c.c. of acetic anhydride and poured into water; the product crystallised from dilute acetic acid in fine, colourless needles, m. p. 196° (Found: C, 72·0; H, 5·5; N, 10·7. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·4; N, 10·5%). *Oxidation of* (IX). This was effected as described in the first example under oxidation of (VIII), except that a fine suspension of the *sulphate* was used, and dark green needles separated at first and disappeared subsequently. Ether extraction gave benzoquinone, yellow needles, m. p. 115°. The other oxidation product was obtained best in a second oxidation in which a further 16 g. of dichromate were added at the air temperature. In this case extraction with ether gave phthalimide, flat, colourless needles, m. p. 234° (confirmed by conversion into phthalamide, colourless crystals, m. p. 222° with evolution of ammonia and reformation of the imide).

N-*Phenylphthalimidine* (XI).—A fine suspension of the sulphate, obtained by grinding 10 g. of the amino-derivative with sulphuric acid, was diazotised with a concentrated solution of 3·6 g. of sodium nitrite. The sparingly soluble *diazo-sulphate*, almost colourless needles, was boiled with 1 litre of alcohol until the evolution of nitrogen had ceased; the *N*-phenylphthalimidine crystallised in almost colourless plates, m. p. 160° as given by Racine (*loc. cit.*)

4′-*Hydroxy*-N-*phenylphthalimidine* (X).—A fine suspension of the hydrochloride, obtained by grinding 20 g. of the amino-derivative with 36 c.c. of concentrated hydrochloric acid and 800 c.c. of water, was diazotised with a concentrated solution of 7·2 g. of sodium nitrite. Carbamide was added to remove excess nitrous acid, the solution poured into 640 c.c. of dilute sulphuric acid (1 : 3) at 90°, and the mixture boiled for 2 hours until the stable diazo-compound had decomposed completely. The hydroxy-

derivative crystallised from alcohol in colourless needles, m. p. 228° (yield 18·2 g.; 90·5%) (Found: C, 74·8; H, 5·1; N, 6·1. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). *Methyl ether.* A solution of 2 g. in 50 c.c. of dry methyl alcohol was boiled with methyl iodide and sodium. The ether crystallised from methyl alcohol in colourless plates, m. p. 134° (Found: C, 75·2; H, 5·5; N, 6·0. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%). The *ethyl ether* crystallised from ethyl alcohol in colourless needles, m. p. 148° (Found: C, 75·7; H, 5·9; N, 5·6. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%).

N-4′-*Nitrophenyliminoisocarbostyril*-3-*carboxylic Acid* (XV).—β-Naphthaquinone (3 g.) was oxidised by calcium hypochlorite to the δ-lactone of *o*-carboxyphenylglyceric acid (2 g.) (XII), colourless leaflets, m. p. 202—203°, as described by Zincke and Scharfenberg (*loc. cit.*), who give m. p. 202°, whereas Bamberger and Kitschelt (*loc. cit.*) give m. p. 204·5°. This acid (12 g.) was heated with concentrated hydrochloric acid (60 c.c.) at 160—165° and gave *iso*coumarin-3-carboxylic acid (8·2 g.) (XIII), colourless, quadrilateral plates, m. p. 238—239° (Zincke, *Ber.*, 1892, **25**, 1493 gives m. p. 235°, whereas Bamberger and Kitschelt give m. p. 237°). An alcoholic solution of *iso*coumarin-3-carboxylic acid (5 g.) and *p*-nitrophenylhydrazine (4·05 g.) was boiled under reflux for ½ hour, and gave o-*carboxy*-α-*hydroxycinnamic acid* p-*nitrophenylhydrazide* (8·5 g.) (XIV), which crystallised from alcohol in fibrous, yellow needles, m. p. 189—190° (decomp.) (Found: C, 55·9; H, 4·0; N, 12·5. $C_{16}H_{13}O_6N_3$ requires C, 56·0; H, 3·8; N, 12·2%). The hydrazide is hydrolysed into its constituents by heating with dilute mineral acids. The elements of water were removed by boiling the finely divided hydrazide (4 g.) suspended in toluene (800 c.c.) with phosphorus trichloride (1 g.) under reflux for 5 hours. N-4′-*Nitrophenyliminoisocarbostyril*-3-*carboxylic acid* (2·24 g.) crystallised from ethyl acetate in small, pale yellow needles, m. p. 287° (decomp.). This compound is formed also by condensing *iso*coumarin-3-carboxylic acid with *p*-nitrophenylhydrazine in presence of phosphorus trichloride and boiling toluene, but the yield is much inferior (Found: C, 58·8; H, 3·6; N, 13·0. $C_{16}H_{11}O_5N_3$ requires C, 59·1; H, 3·4; N, 12·9%). It is readily soluble in acetone or glacial acetic acid, but less soluble in alcohol or ether, and dissolves in alkalis with a deep red colour, the alkaline solution decomposing when heated. It is unaltered by boiling with dilute mineral acids, and is neither esterified nor converted into an anilide when treated under the conditions described for the preparation of these derivatives of 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid (VI). Reduction of the acid (4 g.) with alkaline hydro-

sulphite gave an *amino-acid* (2 g.), almost colourless, crystalline powder, m. p. 265°, which was not examined closely, and no trace of *p*-phenylenediamine could be detected in the reduction mixture.

We desire to thank (1) the Society of Dyers and Colourists for a grant which enabled one of us (A. C. B.) to take part in this investigation, and also for permission to publish the detailed results elsewhere than in the Journal of that Society, (2) Professor F. L. Pyman, F.R.S., for his kindly interest during the progress of the investigation, and (3) Alliance Colour and Chemical Co., British Dyestuffs Corporation, and the Gas Light and Coke Co., for gifts of sodium β-naphthol-1-sulphonate.

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XCVII.—*Absorption Spectra and Tautomerism. Part I. Keto-enol Tautomerism. Ethyl Acetoacetate, Acetylacetone, and α-Benzoylcamphor.*

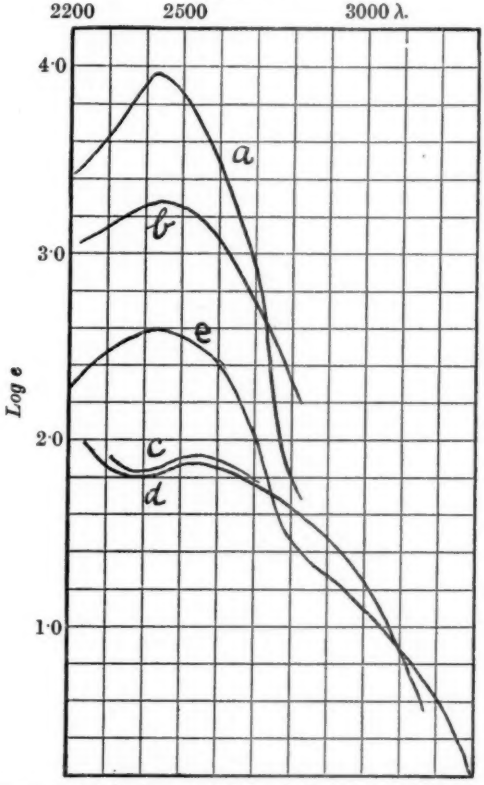
By RICHARD ALAN MORTON and WILLIAM CHARLES VICTOR ROSNEY.

ALTHOUGH the absorption spectra of ethyl acetoacetate and its derivatives have been studied repeatedly (Baly and Desch, J., 1904, **85**, 1029; Stewart and Baly, J., 1906, **89**, 489; Hantzsch, *Ber.*, 1911, **44**, 1771; Hantzsch and Voigt, *Ber.*, 1912, **45**, 85; Baly and Rice, J., 1913, **103**, 91; Morgan and Reilly, J., 1913, **103**, 1494; Bielecki and Henri, *Compt. rend.*, 1913, **156**, 1332; 1914, **158**, 866; *Ber.*, 1913, **46**, 3627; Hantzsch, *Ber.*, 1912, **43**, 3029), a reconsideration of the problem of the origin of their absorption bands is called for in view of the improved experimental methods which are now available (compare Grossmann, *Z. physikal. Chem.*, 1914, **109**, 305).

The vapour from ethyl acetoacetate, cooled to − 80° in order to reduce the vapour pressure, shows an absorption band, without fine structure, at $\lambda_{(max.)} = 2381$ Å., $e_{(max.)} = 1000$ (approx.). Thin layers of the liquid ester show a band at $\lambda_{(max.)} = 2430$, $e_{(max.)} = 367$, and the same band appears in solutions in ether, alcohol ($e = 2000$), and hexane ($e = 9100$). Since the ratio $e_{alcohol}$ to e_{hexane} agrees excellently with the relative content of enol in the solutions as measured by the addition of bromine, the band at 2430 Å. may be ascribed to the enol. This band is shifted to 2550 Å. in ethyl ethylacetoacetate, $CH_3{\cdot}C(OH){:}CEt{\cdot}CO_2Et$, and to 2348 Å. in ethyl β-ethoxycrotonate, $CH_3{\cdot}C(OEt){:}CH{\cdot}CO_2Et$.

Aqueous solutions of ethyl acetoacetate, which appear to be mainly ketonic since they do not absorb bromine appreciably, give a band at 2550 Å., which is nearer to the enolic band than to the undoubtedly ketonic band of acetone at 2747 Å. Its absorptive power, $\epsilon = 81$, is intermediate between those of acetone (17·2) and liquid ethyl acetoacetate (367). Since a displacement of 100 Å. is often produced by a change of solvent, there is as much

FIG. 1.

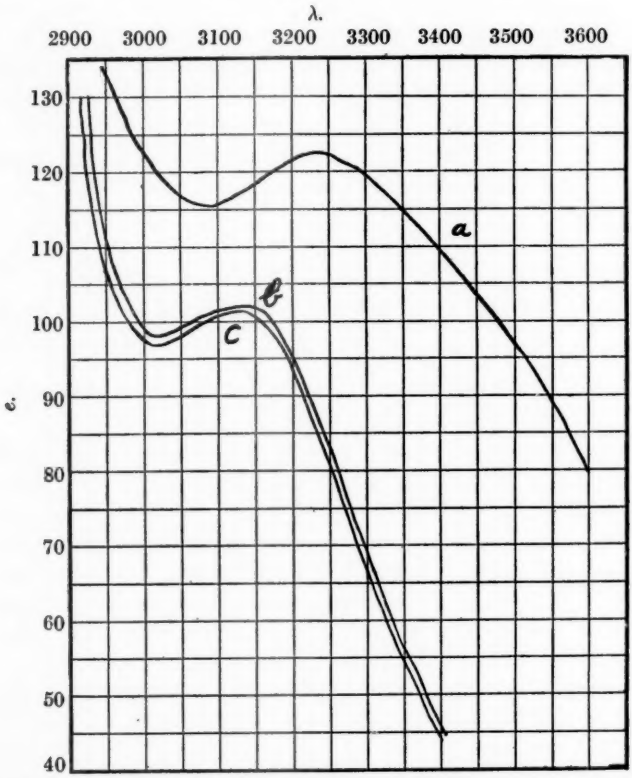


Ethyl acetoacetate (a) in hexane, (b) in alcohol, (c) in dilute hydrochloric acid, (d) in water, (e) liquid.

reason to ascribe the band at 2550 Å. to a trace of enol as to a large amount of ketone. There is, however, an inflexion in the curves for the liquid ester and for its solution in hexane, which may be due to an incipient ketonic band at 2700—2800 Å. This conclusion is confirmed by the fact that the liquid dialkylacetoacetic esters exhibit well-defined bands near 2900 Å., which are weakened on the addition of alcohol, but reappear when alkali is

added. Moreover, analogy with other ketones would lead us to predict a band in ethyl acetoacetate at about 2750 Å. and $\epsilon_{(max.)}$ about 100. Since in hexane, where 80% of the ester is enolic, $\epsilon_{(max.)}$ is 9100, the value for the pure enol must then be about 100 times greater than for the pure ketone. We therefore conclude that the band at 2430 Å. can be attributed to the enolic form and

FIG. 2.



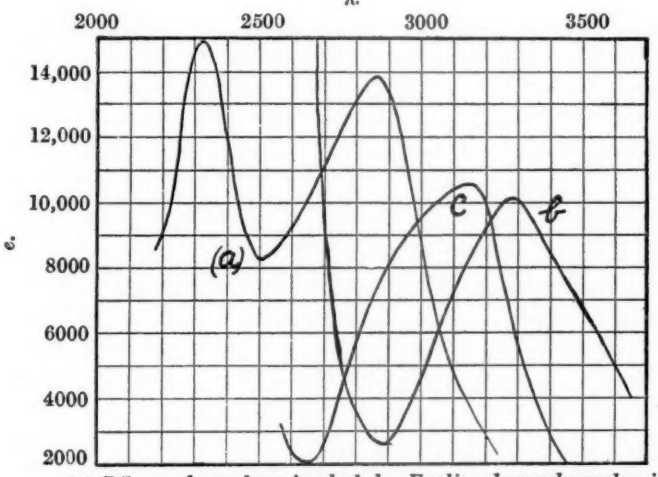
Ketonic α-benzoylcamphor in (a) piperidine, (b) chloroform, and (c) alcohol.

that the ketonic form possesses a weak band near 2700 Å., which is usually masked by the stronger absorption of the enol.

Acetylacetone, which is too absorbent to be examined in the liquid state, gives a strong band at 2750 Å. in aqueous and alcoholic solutions. The ratio of the molecular extinction coefficients, 8920/2200 = 4·05, agrees with the ratio 4·2 of the enol content of these solutions as measured by K. H. Meyer. The band appears, therefore, to be due to the enol, although its wave-length corresponds with that of the acetone band at 2747 Å. Since hexa-

methylacetone shows the usual ketonic band, even when very carefully purified (Rice, *Proc. Roy. Soc.*, 1914, *A*, **91**, 76), and the weak bands of the dimethyl- and diethyl-acetoacetic esters could not have been detected in presence of strongly absorbing enolic impurities, it is clear that the ketonic band cannot be attributed to the presence of a trace of enol in all ketones. It is therefore necessary to conclude that the enolic form of acetylacetone gives a band at the same wave-length as the ketonic form. This conclusion is confirmed by the facts that addition of alkali to acetone (which presumably gives rise to a trace of an enolic salt) increases the intensity of the band but does not produce a new band, and

FIG. 3.



(*a*) *Dibenzoylcamphene in alcohol. Enolic α-benzoylcamphor in* (*b*) *piperidine*, (*c*) *alcohol.*

that the two isomeric forms of benzoylcamphor give bands at the same wave-length but of unequal intensity.

Formation of a new compound from acetone by addition of alkali must result in a redistribution of selective absorption. If the compound exhibits a new absorption band, the number of acetone molecules absorbing at 2747 Å., and therefore $\varepsilon_{(max.)}$, should decrease. The reverse is observed, so that whatever the nature of the new absorbing entity its position of maximum absorption must coincide with that of acetone itself. The data on acetone are thus in agreement with the view that enolic and ketonic modifications possess the same wave-length of maximum absorption. Since the enolic sodium salt can be present only in minute amount,

the enolic form must have a high molecular extinction, as otherwise no increase would have been observed.

The effect of alkali on ethyl acetoacetate and acetylacetone is more complicated, new bands being developed, with high extinction coefficients varying directly as the ratio of alkali to ester up to a molecular ratio of 100 : 1.

Alkaline solutions of ethyl acetoacetate were rapidly neutralised and the bromine addition was measured immediately. Although the nature of the experiments precluded reproducible quantitative data, the concurrent increases of the alkali/ester ratio and of $\epsilon_{(max.)}$ were accompanied by an increased capacity for bromine addition. Hence the bands at 2430 and 2725 Å. for ethyl acetoacetate, and the bands at 2750 and 2913 Å. for acetylacetone, all correspond with enolic substances.

The substitution of potassium, lithium or other metals for sodium causes a small shift in the position of maximum absorption which is roughly proportional to the atomic weight of the substituent. We can therefore infer $\lambda_{(max.)}$ when hydrogen replaces sodium. The position of such a band for ethyl acetoacetate would be nearer 2700 Å. in alcoholic solution, *i.e.*, the enolic ester corresponding with the enolic sodium salt would display the same position of maximum absorption as the ketonic tautomeride. In acetylacetone, the normal ketonic substance has already been shown to absorb at the same wave-length as the ordinary enolic form. The hypothetical enolic form of acetylacetone would, however, show a band different from that of the ketonic form.

Much valuable work has been done in recent years leading to a ringed, chelate, co-ordinated or polar structure for the metallic derivatives of acetylacetone. From the present work, it is evident that the free enolic tautomerides are different from the metallic derivatives in a very distinct way. The free enol does not give the same band as the metallic salts. It therefore seems erroneous to picture the free enol as co-ordinated or ringed in structure (compare Lowry, *Trans. Faraday Soc.*, 1924, **18**, 495, 537).

The views advanced may be subjected to a fairly rigorous test by the isolation and examination of pure ketonic and enolic tautomerides. The isolation of such forms of ethyl acetoacetate can be accomplished by aseptic distillation from evacuated quartz vessels. Unfortunately, it proved quite impossible to retain the purity of thin films of the liquids between quartz plates for the period of time necessary to secure absorption spectra photographs.

The tautomeric forms of benzoylcamphor exhibit the same frequency of maximum absorption, but differ widely in absorptive power. The molecular extinction coefficients of the ketonic form

and of camphor are of the same order (34—100), and the extinctions of the enolic modification and of dibenzoylcamphene are of the order 10,000—14,000. Addition of alkali causes the appearance of a new band, which confirms the view advanced by Lowry that the metallic salts of α-benzoylcamphor are co-ordinated compounds.

Summary of Results.

Substance.	λ (max.).	ε (max.).	Remarks.
Ethyl acetoacetate, vapour .	2381	*ca.* 1000	No fine structure.
„ „ liquid ...	2430	367	
„ „ in ether .	2430	High.	
„ „ in alcohol	2430	2000	Confirming Henri.
„ „ in hexane	2430	9100	„ „
„ „ in water	2550	81·3	„ „
„ „ in dil. HCl	2550	80	
„ „ in NaOH	2725	11,500	Extinction varies as recorded.
Ethyl acetoacetate in alc. NaOEt	2725	29,500	Extinction varies with alkali/ester ratio.
Ethyl acetoacetate in alc. HCl	2430	2,000	
„ „ in dil. aq. KOH	2743	High.	Max. varies with alkali/ester ratio.
Ethyl acetoacetate in LiOH	2707	High.	Max. varies with alkali/ester ratio.
„ „ in piperidine (anhydrous)	2735	150	Low extinction in ketonising solvent.
Cu derivative of ethyl acetoacetate	2736	10,000	
Al derivative in heptane	2684	High.	Extinction of the order 10,000.
„ „ in alcohol	2687	High.	
Mg cmpd. in alcohol	2687	High.	
Ethyl ethylacetoacetate, pure liquid	2550	400	
Ethyl ethylacetoacetate in alcohol	2550	680	Henri records max. at 2341.
Ethyl ethylacetoacetate in water	2700	Low.	
Ethyl ethylacetoacetate in dil. NaOH	2740	10,000	
Ethyl ethylacetoacetate in alc. NaOEt	2810	20,000	
Ethyl ethylacetoacetate in piperidine	2695	Uncertain.	
Ethyl ethylacetoacetate, vapour	*ca.* 2380		No fine structure.
Ethyl methylacetoacetate in alcohol	2520		Hantzsch's data (*loc. cit.*) measured from published curves.
Ethyl methylacetoacetate in water	2680		
Ethyl methylacetoacetate in alkali	2825		
Ethyl β-ethoxycrotonate, vapour	2275	Uncertain.	

Substance.	λ (max.).	ε (max.).	Remarks.
Ethyl β-ethoxycrotonate, liquid	Indications of band near 2050.		
Ethyl β-ethoxycrotonate in alcohol	2348	2880	
Ethyl β-ethoxycrotonate in alc. NaOEt	2348	1820	
Ethyl dimethylacetoacetate, liquid	2837	Low.	Film too thin to allow of reproducible values of ε.
Ethyl dimethylacetoacetate in alcohol	Inflexion only.		
Ethyl dimethylacetoacetate in alc. NaOEt	2840		
Ethyl dimethylacetoacetate in water	Inflexion only.		
Ethyl dimethylacetoacetate in aq. NaOH	2760		
Ethyl dimethylacetoacetate in piperidine	Inflexion only.		
Ethyl diethylacetoacetate, liquid	2848	Low.	
Ethyl diethylacetoacetate in alcohol, water, or piperidine	Inflexions only.		
Ethyl diethylacetoacetate in aq. NaOH	2762		
Ethyl diethylacetoacetate in alc. NaOEt	2850		
Acetylacetone, liquid	Continuous end absorption.		
„ in water	2750	2200	
„ in alcohol	2748	9000	
„ in dil. HCl	2750	2000	
„ in aq. LiOH	2917		
„ in aq. NaOH	2926	Order 20,000	Extinction varies with alkali/ester ratio.
„ in aq. KOH	2935		
„ in aq. RbOH	2967		
„ in piperidine (anhydrous)	2955	Not measured owing to difficulties of manipulation.	
„ in alc. NaOEt	2927	19,500	
Camphor in alcohol	2840	34	
Dibenzoylcamphene in alcohol	2860	13,700	
	2365	15,100	
α-Benzoylcamphor, ketonic modification in alcohol	3130–3145	103	
α-Benzoylcamphor, ketonic modification in chloroform	3125	104	
α-Benzoylcamphor, ketonic modification in piperidine	3240	123	
α-Benzoylcamphor, enolic modification in alcohol	3150	10,600	
α-Benzoylcamphor, enolic modification in piperidine	3280	10,300	
α-Benzoylcamphor, enolic modification in alc. NaOEt	3275	15,250	
Benzoylcamphor, ketonic modification freshly dissolved in alc. NaOEt	3072	1380	
	2750	1040	
Same solution after standing	3275	4000	
Same solution after some days	3270	12,300	

The following maxima have been measured for metallic derivatives of acetylacetone :

Metal.	Solvent.	λ (max.).			Metal.	Solvent.	λ (max.).
Cu	Alcohol	2435 and 2965			Th	Alcohol	2840
,,	Heptane	2445	2970		,,	Heptane	2735
Be	Alcohol	2930			,,	Ammonia + alcohol	2960 2960
Fe^{III}	Alcohol	2730	3525	4350			
,,	Heptane	2720	3527	4340	Al	Alcohol	2893
Mg	Alcohol	2837			,,	Heptane	2875

Some of the results are recorded as supplementing the work of Lowry and Desch (J., 1909, **95**, 807), Morgan and Moss (J., 1914, **105**, 189), and French (*Proc. Roy. Soc.*, 1924, *A*, **106**, 489).

The present investigation was completed before the appearance of Grossmann's work (*loc. cit*). Whilst our experimental data are on the whole in excellent agreement with those of this investigator, some important differences may be noted. Grossmann does not record the fact that thin films of ethyl acetoacetate exhibit a band at 2430 Å., and the existence of a band in the dialkylacetoacetic esters appears to have escaped his notice.

We wish to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for maintenance grants during a part of the time occupied by the work, and to Professor E. C. C. Baly, C.B.E., F.R.S., for much guidance and encouragement.

THE UNIVERSITY, LIVERPOOL. [*Received, December 16th,* 1925.]

XCVIII. — *Absorption Spectra and Tautomerism. Part II. Ethyl Mesityloxidoxalate, Formylphenylacetate, and Diacetylsuccinate.*

By RICHARD ALAN MORTON and EDWARD ROGERS.

Ethyl Mesityloxidoxalate.

THREE modifications of ethyl mesityloxidoxalate have been isolated : (i) α, m. p. 21° ; (ii) β, m. p. 59—60° ; (iii) a dimeric form, m. p. 175° (Federlin, *Annalen*, 1907, **356**, 261). These can be converted into one another as follows :

$\beta \rightleftarrows \alpha$ in the dark, equilibrium being reached after about 12 weeks.

$\alpha \longrightarrow \beta \longrightarrow$ dimeride in diffuse daylight, with precipitation of the dimeride from most solvents.

The α-form develops a red colour with ferric chloride and is undoubtedly the enolic form (I). Claisen at first regarded the

β-form as a dihydropyrone derivative (III) (*Ber.*, 1891, **24**, 116), but later he formulated it as the ketone (II).

(I.) $CMe_2{:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et$.
(II.) $CMe_2{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$.

(III.) $CO\langle\begin{matrix}CH_2\text{——}CMe_2\\CH{:}C(CO_2Et)\end{matrix}\rangle O$

Dieckmann (*Ber.*, 1920, **53**, 1772) regards the α-form as enolic, but rejects the ketonic formula for the β-form, on the ground that the small percentage of enol in the equilibrium mixture is not in accordance with Claisen's rule that the velocity of enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups: moreover, the α-ester when distilled passes mainly into the β-ester. Dieckmann and von Auwers (*Ber.*, 1923, **56**, 1527) regard the refractometric data for the fused material as confirming the structure (III), and Borsche and Thiele (*Ber.*, 1923, **56**, 2132) find further confirmation in the fact that the catalytic hydrogenation of the α-ester is more rapid than that of the β-ester.

This example of tautomerism is interesting in several respects.

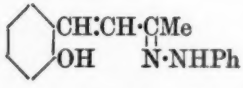
(1) The equilibrium can be studied either as a reversible or as an irreversible one.

(2) The β-form can be examined under conditions such that the enolic tautomeride is excluded.

(3) The relatively slow rate of change renders the course of the reactions amenable to spectrographic investigation.

In the preceding paper definite conclusions have been drawn concerning the absorption spectra of keto-enol tautomerides. The results of an examination of ring-chain tautomerides are now recorded. We are greatly indebted to Dr. A. McGookin of this University, who suggested and synthesised the compounds of this nature.

Spectrographic evidence shows that keto-enol tautomerides exhibit absorption maxima at the same wave-length but with differing absorptive power. In the cases of pure ring-chain tautomerism without elimination of water, *e.g.*,

(IV.)  (V.)

(IV) shows two bands at 3600 Å. and 2545 Å. and (V) shows one band at 2790 Å. Ring-chain tautomerides thus differ markedly from keto-enol tautomerides in absorption spectra.

The dimeric modification of ethyl mesityloxidoxalate shows no selective absorption and the continuous absorption is relatively feeble, so that the presence of this form does not seriously interfere with the absorption of the β-form in various solvents.

The β-form in alcohol, hexane, or chloroform shows a well-defined band of high extinction coefficient, with λ (max.) varying a little for the different solvents. The enolic modification shows another band of high extinction coefficient, and a less noticeable shift due to the solvent. When a solution of the α-form in any of the three solvents used was kept, the position of maximum absorption shifted towards the ultra-violet and the measured absorption curve was the sum of the curves due to the α- and β-forms.

The β-form in presence of alkali shows three bands at λ (max.) 3512, 2867, and 2450—2500 Å. The first and the third are developed when alkali is added to the α-(enolic) modification and are also shown by the pure sodium derivative. If alkali is added to the β-form, the system will contain unchanged β-ester and the sodium salt of the α-ester. Hence the observed curve is a summation of two curves, one with a maximum at 2825 Å. due to the β-ester and the other with maxima at 3510 and 2457 Å., due to the sodium derivative of the α-ester.

An alcoholic solution of the β-compound to which a large excess of sodium ethoxide had been added was left on ice. Later it was saturated with dry hydrogen chloride, and the sodium chloride filtered off. The solution then showed only one band, namely, the 3120 band due to the enolic ester.

The spectrographic data show that the reversible $\alpha \rightleftharpoons \beta$ isomerism of ethyl mesityloxidoxalate resembles ring-chain tautomerism rather than keto-enol tautomerism. This conclusion is in agreement with the most recent chemical evidence. The metallic derivatives are probably co-ordinated compounds.

Summary of Results.

Substance.	λ (max.).	ε (max.).	λ (min.).	ε (min.).
Ethyl β-mesityloxidoxalate :				
Fresh solution in alcohol ...	2825	12,200	2275	3800
„ „ „ hexane ...	2775	11,500	2310	3300
„ „ „ chloroform	2850	11,500	2460	3700
Alcoholic solution plus 10 equivs. of NaOEt	3512	13,000	3010	3700
	2867	7,500	2320	3400
	2495	7,500	—	—
Ethyl α-mesityloxidoxalate :				
Fresh solution in alcohol ...	3125	14,200	2415	3950
„ „ „ hexane ...	3122	14,000	2420	3900
„ „ „ chloroform	3125	15,100	2475	4750
Alcoholic solution plus 1 equiv. of NaOEt	3510	16,500	2825	3500
	2457	6,750	—	—
10 equivs. „	3510	18,700	2825	3750
	2457	9,200	—	—
100 equivs. „	3510	21,250	2870	3800
	2457	9,200	—	—

Ethyl Formylphenylacetate.

Four forms of this substance have been recorded:

(1) Liquid, b. p. 135°/15 mm.; enolic.
(2) Solid, m. p. 70°; regarded as an aldo-form or as a geometrical isomeride of (3).
(3) Solid, m. p. 100—110°.
(4) Solid, m. p. 50° (Michael's modification .

Doubtless these forms are not all isomerides. Wolf (*J. Physical Chem.*, 1900, **4**, 123) has shown that by keeping the ester at different temperatures for long periods it can be made to melt at any temperature between 50° and 100°, the former temperature being a stable triple point in the phase diagram. The difference in m. p. and refractivity of the various forms is due to one or more of the alternatives: (1) keto-enol tautomerism, (2) stereoisomerism, (3) unequal degrees of association. Michael and Fuller (*Annalen*, 1912, **391**, 275) have adduced evidence that all the forms are unimolecular. The conclusion is drawn that only three forms exist having b. p. 125°/9 mm., m. p. 40°, and m. p. 100—103°, respectively, all of which are enolic, since they react with aliphatic tertiary amines.

Wislicenus, however, after studying the isomerism of ethyl formylphenylacetate over a period of 30 years, draws the conclusion that the only two forms possessing real existence are (α), b. p. 125—126°/9 mm., and (β), m. p. 103—105°. All other "forms" he regards as mixtures of the α- and the β-form. These he considers, after reviewing all the available evidence, to be *cis*- and *trans*-isomerides.

Together with his pupils he has studied the methyl formylphenylacetates and has found two modifications: (α), m. p. 40—41°, and (β), m. p. 91—93°. No mixtures occur.

The α-modification is undoubtedly enolic, but the β-form presents difficulties, since it is doubtful whether it exists as an aldo-form or as a geometrical isomeride of the α-form. The two modifications react differently with copper acetate, and the β-form will under no conditions develop a coloration with ferric chloride. The anilides and piperidides of formylphenylacetic acid give two modifications, both of which are enolic. Michael considers that the aldo-modification has never been isolated and that much of the earlier work was misinterpreted owing to the fact that the β-form can add on a molecule of alcohol. For example, methyl formylphenylacetate–

methyl alcoholate is a crystalline substance, m. p. 89—92°, which does not develop a colour with ferric chloride.

Dieckmann (*Ber.*, 1917, **50**, 1375) concludes that the ethyl ester exists in the pure state only as a liquid enol, α, and a solid, m. p. 110°, which also is enolic.

Preparations of ethyl formylphenylacetate were examined having b. p. 127°/10 mm., m. p. 70°, and m. p. 100°, respectively. No maxima were found in the absorption curves, which were similar in extinction coefficient (order 7500 at 2600 Å.) and inflexions (2600—2100). With alkali, a definite band was obtained with a maximum at 2740 (*e* max. 19,200, 22,200, 16,800).

The interpretation of these results is somewhat difficult. Although ketones show well-defined maxima, in this substance the carbonyl group is a part of the formyl radical, so that the absence of the ketonic band does not prove the non-existence of an aldo-form. The data do not show the very large variations of *e* which are observed in keto-enol tautomerism. The absorptive powers of *cis*- and *trans*-isomerides (Errara and Henri, *Compt. rend.*, 1925, **181**, 549) for a given wave-length are in the ratio 1 : 1—2, generally near 1·0—1·2. This is precisely the kind of variation observed in ethyl formylphenylacetate. Hence the spectrographic data strongly support the conclusion that the isomerism of this substance is of the *cis*- and *trans*-variety.

Ethyl Diacetylsuccinate.

The isomerism of this ester has been the subject of much controversy. Two definite modifications were isolated and examined spectrographically :

Isomeride, m.p. 92°; λ (max.) = 2490, *e* (max.) 7600.
Isomeride, m. p. 31°; λ (max.) = 2490, *e* (max.) 6250.

With alkali both forms exhibit a band at λ = 2750 (*e* max. varying with the alkali/ester ratio).

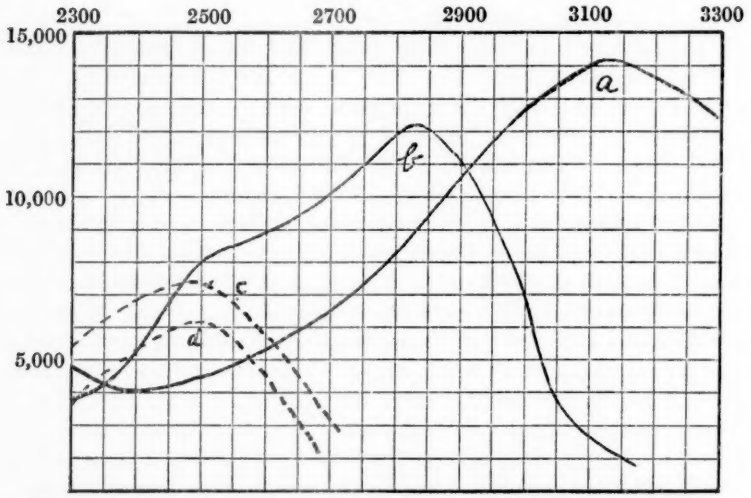
The two substances provide an interesting comparison with ethyl acetoacetate :

	Acetoacetate.	Diacetylsuccinate.
Enol band	2430Å.; *e*, 10,000	2490Å.; *e*, 7600 6250
Keto band	2700Å. app.; *e* order 100.	unknown.
Co-ordinated sodium salt	λ (max.) 2725.	λ (max.) 2750.
Ratio of extinctions	enol/keto = 100 : 1 (order)	m.p. 92°/m.p. 31° = 1·22.

The following results are from Henri and Errara's work. The

figures denote the ratio of ϵ for the *trans*-isomeride to ϵ for the *cis*-isomeride at the wave-lengths cited.

FIG. 1.



(*a*) *Ethyl α-mesityloxidoxalate in alcohol.* (*b*) *Ethyl β-mesityloxidoxalate in alcohol.* (*c*) *Ethyl diacetylsuccinate, m. p.* 92°, *in alcohol.* (*d*) *Ethyl diacetylsuccinate, m. p.* 31°, *in alcohol.*

Substances.	λ 2520Å.	λ 2410Å.
CHCl:CHCl	1·4	2
CHEt:CHBr	1·15	1·2
CHMe:CHBr	1·5	1·5
CHI:CHCl	1·3	1·25

Hence the data provide strong support for the view that the isomerism of ethyl diacetylsuccinate is of the *cis-trans* type.

One of us (E. R.) wishes to express his gratitude to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant. We are very grateful to Professor E. C. C. Baly, C.B.E., F.R.S., whose advice and encouragement have been of great value to us.

THE UNIVERSITY, LIVERPOOL. [*Received, December* 16*th*, 1925.]

XCIX.—*Absorption Spectra of Mesityl Oxide.*

By Richard Alan Morton.

Harries (*Ber.*, 1899, **32**, 1329; *Annalen*, 1904, **330**, 189) has stated that when mesityl oxide was shaken for 36 hours with a 40% solution of sodium bisulphite, 30% of the material remained unchanged. The residue obtained after shaking five times with fresh solutions of sodium bisulphite showed a refractive index and a density differing in the third decimal place from those of the original ketone. It appeared, nevertheless, to be mesityl oxide, since it yielded the same *cis*- and *trans*-oximes. Since the mesityl oxide regenerated from the bisulphite compound reacted completely with fresh sodium bisulphite, Harries concluded that the phenomena were not due to tautomeric equilibrium but to a new type of isomerism. Experiments were therefore made in order to determine whether the absorption spectrum of the inactive form differs from that of ordinary mesityl oxide.

Mesityl oxide synthesised from acetone by means of hydrogen chloride proved to be spectroscopically identical with the redistilled commercial material, b. p. 128°, which was used in an attempt to repeat the work of Harries. The results were as follow:

(1) The whole of the mesityl oxide reacted with sodium bisulphite.

(2) The yield of double compound was practically quantitative.

(3) The ketone regenerated from the bisulphite compound was identical with the original product in respect of (*a*) boiling point, (*b*) absorption spectrum in the liquid state, (*c*) absorption spectrum in alcoholic solution.

(4) Earlier results (Henri and Bielecki, *Compt. rend.*, 1914, **158**, 567, 866, 1022; Purvis and McCleland, J., 1913, **103**, 433) were confirmed.

(5) Four distinct absorption bands were found. Shifts due to solvent occurred, but none due to vapour–liquid, the pure liquid ketone showing the same frequency of maximum absorption as the vapour.

Summary of Data.

	Present work.		
	λ max. Å.	ε max.	Other work.
Vapour	3239	low	Purvis and McCleland found λ max. = 3238.
Liquid	3240	58	—
Alcoholic solution	3130	55	Henri and Bielecki found max. = 2360.
	2380	14,000	
Aqueous solution	2440	11,000	—
Hexane solution	3272	56	—
	2348	14,000	2335
Heptane solution	3275	50	—
	2330	14,000	—

It must be concluded that some unrecorded factor entered into the work of Harries.

I wish to express my thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for his interest and advice.

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C.—*Studies of Dynamic Isomerism. Part XXI. The Velocity of Mutarotation of Tetramethylglucose and of Tetra-acetylglucose in Aqueous Acetone.*

By GRIFFITH GLYN JONES and THOMAS MARTIN LOWRY.

ALTHOUGH it has long been known that water is an effective catalyst for the mutarotation of the sugars, even apart from the presence of basic or acidic impurities (see Part I, J., 1903, **83**, 1314), there was until recently no clear picture available as to the way in which the water intervenes in order to determine the changes of structure which give rise to the observed changes of rotatory power. In particular, although it was known that the formation of a hydrate does not bring about any marked alteration of the rotatory power of α-glucose, and cannot therefore be a direct cause of the mutarotation of this sugar (Part III, J., 1904, **85**, 1551), there were no experimental data to show how the subsequent molecular rearrangement of the hydrate was effected. It was suggested, however, in a recent paper (Part XVIII, J., 1925, **127**, 1371) that there is a marked analogy between the conditions under which mutarotation occurs and those which are used to promote the hydrolysis of an ester, and that, since mixtures of acids and bases with water are even more efficient catalysts than water itself, the action of the water probably depends on its amphoteric properties. If this view were correct, any solvent which can accept a proton from the sugar, and return it to the sugar residue, might act as a complete catalyst for the mutarotation. This conclusion has been verified (Part XX, J., 1925, **127**, 2883) by the discovery that an anhydrous mixture of pyridine and cresol is an excellent catalyst for the mutarotation of tetramethylglucose.

The experiments now described were undertaken in order to secure information in reference to solvents which appear to diminish the catalytic activity of water instead of increasing it. The choice of acetone as a diluent was dictated by the fact that Irvine (J., 1913, **103**, 584) has found it to be a particularly easy solvent in which to effect an arrest of mutarotation in a methylated sugar. It was thought that this might be due to some restraining action of the